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Vol. 198 OCTOBER, 1924 No. 4

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Journal of The Franklin Institute

1924

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Published Monthly by

THE FRANKLIN INSTITUTE OF THE STATE OF PENNSYLVANIA, PHILADELPHIA

SIX DOLLARS PER YEAR (Foreign Postage Additional) SINGLE NUMBERS, SIXTY CENTS

Entered at the Post Office at Philadelphia, Pa., as second-class matter.

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Vol. 198 OCTOBER, 1924 No. 4

MINIMAL LENGTH ARC CHARACTERISTICS.*

BY

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Member of the Institute.

INTRODUCTORY—ARC CHARACTERISTICS.

THE relationship between voltage and current in a stable electric arc is represented in rectangular coördinates by what is known as the arc characteristic—more completely, the family of arc characteristics for various arc-lengths. Such a set of representative characteristic curves for carbon electrodes is shown in Fig. 1. The characteristic curves are approximately hyperbolæ in which high values of current correspond to low values of voltage and *vice versa*. The characteristic curves for large arc-lengths lie farthest out from the origin of coördinates, and as the arc-length is decreased, the curves move in toward both current and voltage axes.

Arc characteristics are commonly held to conform closely to the equation

$$e = \alpha + \beta l + \frac{\gamma l + \delta}{i^n}$$

where e is the voltage across the arc, i is the current, l is the arc-length, α, β, γ, δ and n are constants. This equation holds quite well for carbon with the value unity for the constant n, and fairly well for other electrode materials with lower values of n, *provided*

* Communicated by the Author.

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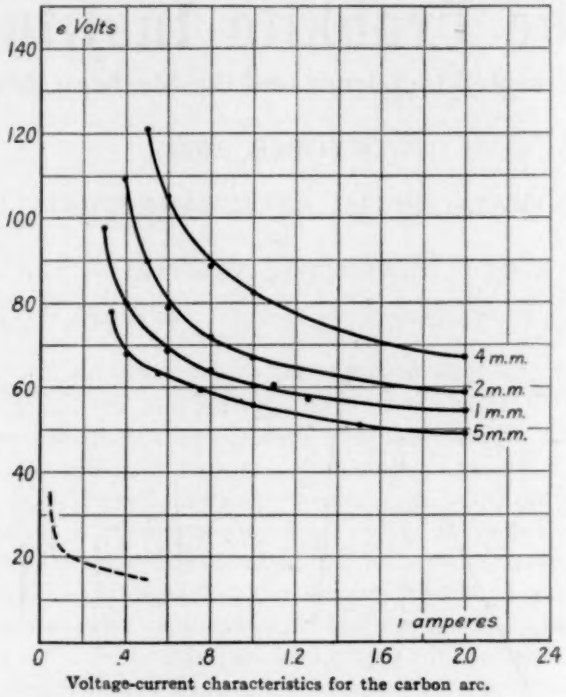
the arcs are at least several millimetres long; for shorter arcs more complicated equations are demanded.[1]

Inspection of this equation shows that if the current is held constant there should be a linear relation between e and l, and

FIG. 1.



Voltage-current characteristics for the carbon arc.

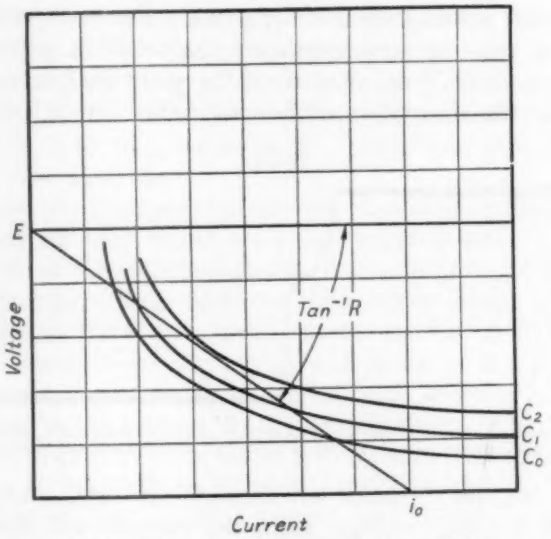
that the limiting condition as l approaches zero is an arc of characteristic

$$e = \alpha + \frac{\delta}{i^m}$$

The first conclusion is not entirely borne out by experiment: As the arc-length becomes quite small the voltage falls off more rapidly than the linear relation calls for. Nevertheless a *limiting value* for the arc-voltage, not zero, is indicated by any reasonable extrapolation for *zero length*. The series of such limiting values with their corresponding currents constitute what may be called the zero length, or *minimal length*, arc characteristic. The existence of this characteristic is thus in the first place inferred by

extrapolation from finite length arc characteristics. It is one of the objects of this paper to investigate certain consequences of this inference; to see whether experimental test reveals phenomena in accord with the conception of a minimal or zero length arc. The consequences to be investigated are specifically those to be

FIG. 2.



Voltage-current relations in an opening contact.

drawn as to the nature of the discharge at separating contacts, or *break arcs.*

THE BREAK ARC.

If we grant the reality of the zero length characteristic as part of the family of arc characteristics, it is a straightforward matter to infer what should be the voltage-current relation at any instant in the discharge between electrodes which are changing their relative separation.

Let us suppose that, with the electrodes in contact, a current i_0 is flowing. Let the electromotive force be designated by E, and the resistance in series with the contact by R. Suppose now the electrodes are separated: The ohmic resistance of the contact will rise from its initial value to infinity in a time which for any practical method of opening the contact will be exceedingly short. If no arc is struck, we shall have at any instant the following

relation between e_k, the voltage across the contact, and i_k, the current through the contact:

$$e_k = E - Ri_k$$

that is, the relation between voltage and current is represented by a straight line as shown in Fig. 2.

If, however, during the process of opening, the voltage and current attain values such that the straight line representing their relationship cuts the zero length arc characteristic (straight line i_o E and curve C_o, Fig. 2) then at the point of intersection the current has the alternative of flowing either through the ohmic

FIG. 3.

Oscillogram of break arc current showing quick drop to the arc characteristic, persistence of arc for a finite period, and abrupt fall of current to zero as arc is extinguished.

resistance of the contact or through an arc. As the arc constitutes a lower voltage path, the current will flow as an arc discharge.

If now the electrode separation remains so small that the corresponding arc characteristic differs but little from the zero length characteristic, a stable arc will persist. This is because when the resistance R is great enough for the straight line mentioned to cut the arc characteristic, it is also great enough for the arc to be stable, in conformity with the well-known condition of stability (Blondel, Kaufmann). If the electrodes are separated further, the arc will persist to greater lengths as long as R is great enough to insure its stability (C_1), but ultimately a length will be attained such that the arc can no longer exist and it will be extinguished (C_2). The complete course of events occurring during the separation of a pair of electrodes between which an arc is struck, should then be as follows: First, an abrupt drop in the current, accompanied by an abrupt rise in the voltage across the contact; second, the striking of an arc, shown on any instan-

taneous record of current and voltage by the occurrence of a current of value lower than the initial current which is broken, this current persisting for a longer or shorter time, depending upon the value of electromotive force and resistance, and decreasing in value as the electrodes continue to separate (at a rate very much slower than the initial drop due to the changing ohmic resistance of the contact), the voltage at the same time rising; third, the current drops abruptly to zero, and the voltage rises simultaneously to the value of the electromotive force.

The oscillogram (Fig. 3) shows quite clearly that the predicted process does in fact occur when a discharge passes between opening contacts, and thus supports the conception of a true zero length arc characteristic.

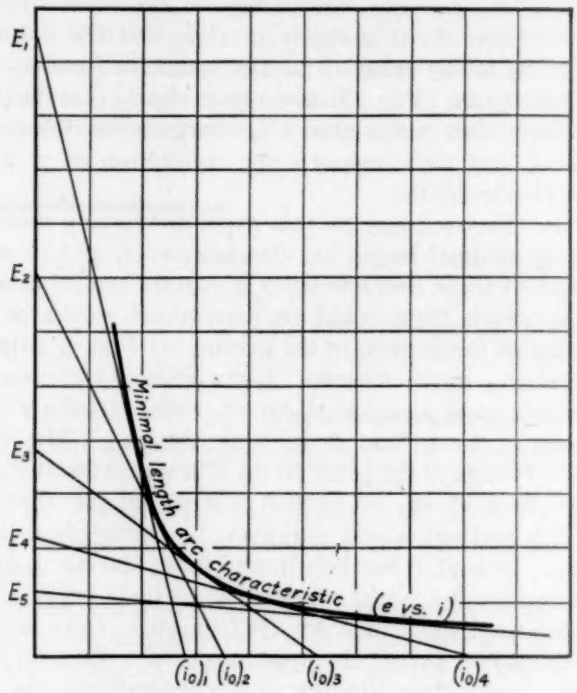
It is the chief purpose of this paper to develop methods for determining minimal length arc characteristics, and to study the peculiarities of these characteristics in certain typical cases. One method by which these could be determined would be to take oscillograms of break arcs, in the manner of Fig. 3, with continually decreasing initial currents, for a series of chosen electromotive forces, until a series of curves, each showing a just perceptible step in the current drop, were obtained. The values of current and voltage at the point on the film where the step occurred could then be read off, to furnish a point on the characteristic curve. This method would, however, be cumbersome and time consuming. Instead, it has been found most feasible to determine the characteristics by *visual observation* of these break arcs, finding the limiting conditions of electromotive force and initial current which just permit the appearance of a flash on breaking the circuit. From these limiting electrical conditions the minimal length arc characteristic can be derived by utilization of the relations shown in Fig. 2, in a manner explained in the next section.

DETERMINATION OF VOLTAGE-CURRENT CHARACTERISTICS FROM THE BREAK ARC; METHODS AND APPARATUS.

Two methods of obtaining the break arc have been used in this work, both giving the minimal length characteristics when the limiting conditions for the arc's appearance are analyzed. The first of these uses a practically non-inductive circuit, in which the electromotive force and current may be changed at will. The experimental data as obtained consist of pairs of values of initial

current i_o, and electromotive force E at which the break arc just appears. We then plot the points (i_o, o) on the x-axis and the points (o, E) on the y-axis of a coördinate system. The straight lines connecting corresponding points form a family which envelops the arc characteristic curve, as shown diagrammatically

FIG. 4.



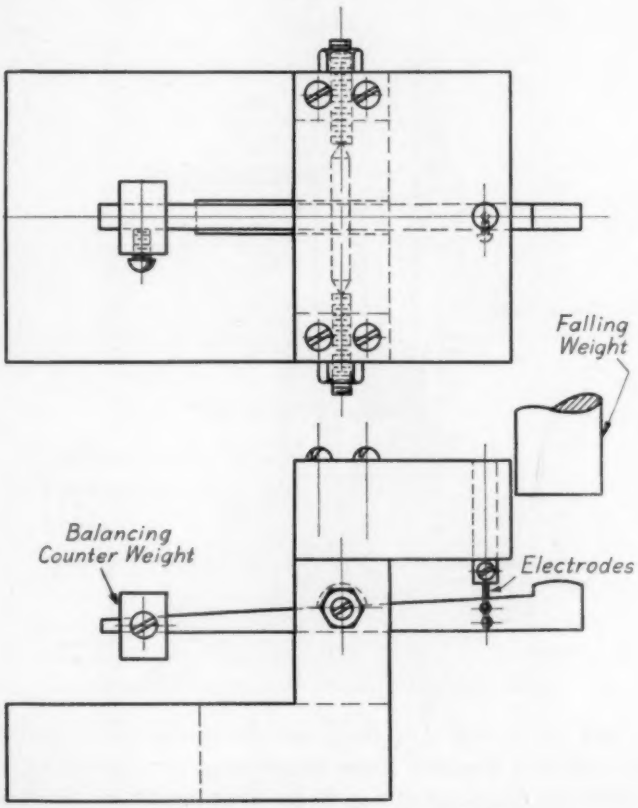
Method of deriving minimal length arc characteristics from limiting values of E and i_o.

in Fig. 4. A practical disadvantage of this method is that it requires the use of comparatively high electromotive forces to handle the small currents which are of particular interest.

The second method which has been used will be spoken of here commonly as the method of *critical shunted resistance*. In this method a highly inductive circuit is used, that is, half a henry or more in series with the contact, while the steadily applied electromotive force may be quite low, usually not more than 10 or 12 volts for the experiments described below. Shunted across the contact is a variable non-inductive resistance. The value of the

inductance is such that when the contact is open, the current through the whole circuit is maintained at practically its initial value for the whole time with which we are concerned. This method is available because the voltage-current relation for the contact inserted in such a circuit is of the same analytical form as

FIG. 5.



Contact device operated by falling weight.

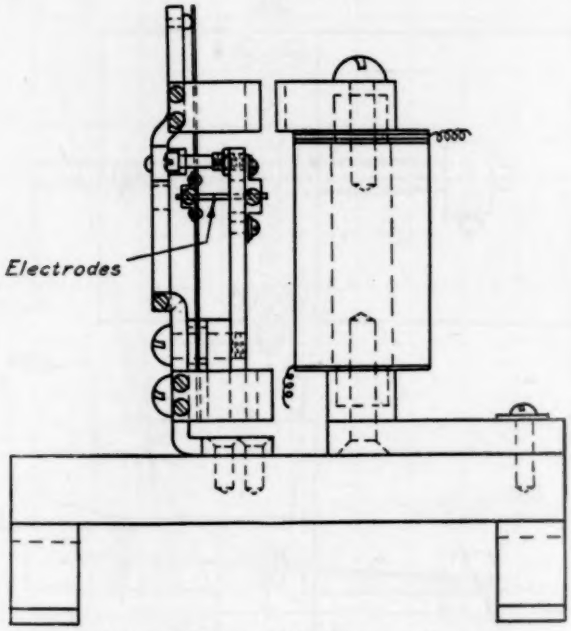
the voltage-current relation for the contact in the non-inductive circuit previously described. For, representing by R_s and i_s the shunted resistance and the current through it, by i_k the current through the contact, and by i_o the sum of these:

$$e_k = R_s i_s = R_s (i_o - i_k) = R_s i_o - R_s i_k$$

and this is identical in form with the second equation of the

introductory section with R replaced by R_s and E replaced by $R_s i_o$. The experimental data as obtained consist of pairs of values of i_o and of the shunted resistance at which the break arc just appears (the critical shunted resistance), forming curves which, as will be shown below, are in general convex toward the origin of coördinates. We then plot the points (i_o, o) on the

FIG. 6.



Special magnetically operated relay for contact study.

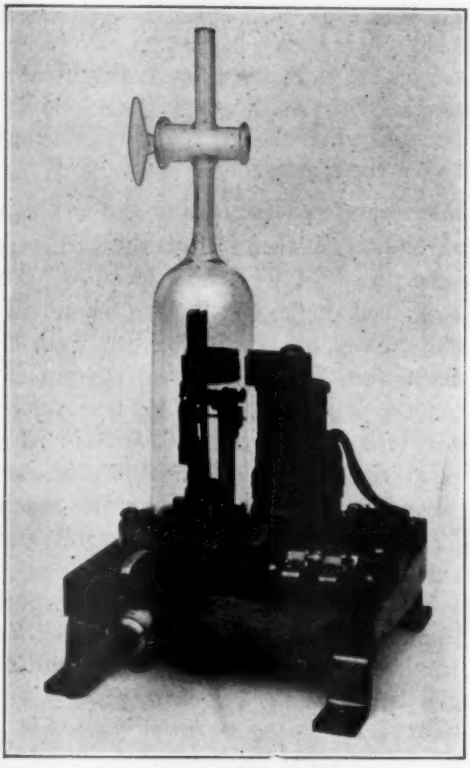
x-axis and the points $(o, R_s i_o)$ on the y-axis of a coördinate system, and the straight lines connecting corresponding points envelop the arc characteristic as in the previous case.

Either of the methods just described suffers under the disadvantage as compared with the ordinary method of obtaining static arcs, that with currents for which the voltages are changing but little, the critical conditions can only be attained by breaking very large currents. In the present work, this has meant the restriction of the minimal length characteristics to current values of an ampere or less. This is not, however, a serious limitation,

since in telephone engineering, in connection with which the work was done, the majority of currents are below this value.

The apparatus used in the investigation consisted of special devices arranged to bring about the contact and separation of

FIG. 7.



Special relay enclosed in bell-jar.

short rods of various materials. One of these devices, shown in Fig. 5, carries one of the electrodes in a lever of the second class operated by a falling weight, the other electrode being held in a fixed position. The clamping screws by which the rods are held permit the easy substitution of other materials. With this apparatus very sharp breaks could be obtained, and the velocity of separation could be controlled by the height of fall of the weight. The second form of apparatus used was a special magnetically

operated spring relay, which is shown in Fig. 6. This relay was developed for general study of the behavior of contact materials under conditions of make and break simulating those in commercial relays while, however, permitting the insertion of materials of any desired composition in a way not possible in the commercial devices. It is also designed so that a small bell-jar may be placed over it and the contacts operated in different gases. The apparatus enclosed in the bell-jar is shown in Fig. 7.

The electrodes were in all cases short cylindrical rods of 1 mm. diameter. In some of the oscillographic work, collars of insulating material were placed on the electrodes to prevent the discharge striking back over their sides.

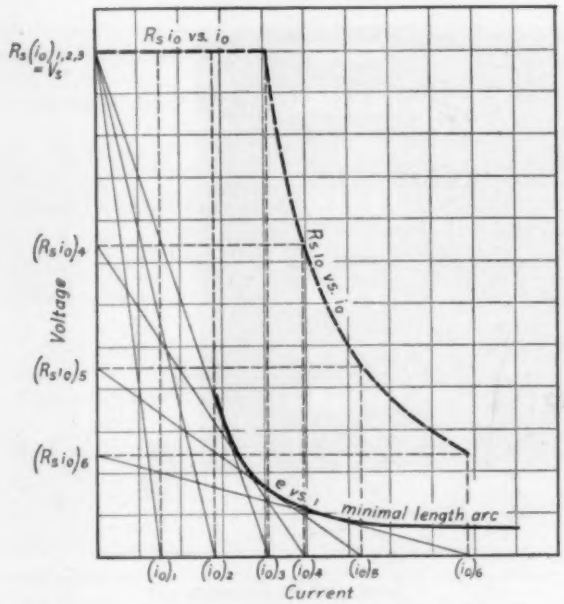
DISTINCTION BETWEEN THE BREAK ARC AND THE BREAK SPARK.

The typical relation between critical shunted resistance R_s and the current i_0, determined by the method of critical shunted resistance as described in the last section, is shown in a number of experimental curves of which Fig. 14 (air data) may be selected for discussion. As the critical current is increased in value from zero, the value of the shunted resistance falls steadily. However, at a certain value of current which is different for each electrode material, *the curve breaks abruptly into a second curve* which is roughly of similar appearance but lies much closer to the current axis. This *break point* and its interpretation are of great importance in this investigation.

Upon studying the various features of these broken curves, it was established quite early that we had here two different kinds of discharges. In the upper arm of the compound curve, that is, for lower initial currents, *the product of $R_s i_0$ is very nearly a constant, which with air as the surrounding gas is 300.* For the curve for larger initial currents, beyond the break point, no such relationship holds. This immediately suggests that the discharge occurring on breaking the smaller currents is a true *spark*, that is, a disruptive discharge through the environing atmosphere, and that the true break arc, which it is our purpose to investigate, only makes its appearance, by this method of study, for the higher currents. In terms of the voltage-current relationship, this means that as the current through the contact decreases, the voltage, in rising, does not cross the zero length arc characteristic, but that its final value is above the atmospheric breakdown voltage.

According to this interpretation, the voltage at which the low current discharge before the "break point" occurs should be uniformly about 300, while beyond the break point the actual voltage across the discharge should not only be very much less, but should no longer be equal to the product of shunted resistance by current. The latter product, then, merely represents the terminal value of the voltage while the discharge actually takes place somewhere

FIG. 8.



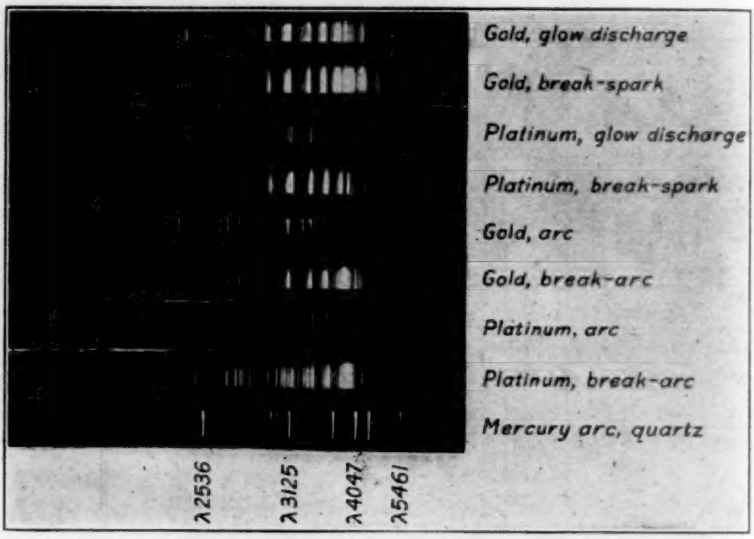
Relation of final voltage to discharge voltage in the arc and in the spark.

between zero voltage and this terminal value. The conditions below and above the break point, according to this view, are shown in Fig. 8, where $(i_o)_1$, $(i_o)_2$ are initial currents which just give a true spark when broken and for which $R_s i_o = 300$ is the true voltage of the discharge. $(i_o)_3$ is an initial current which gives a "spark" for the same value of $R_s i_o$, but, since the line $(i_o)_3 R_s$ cuts the arc characteristic, the discharge actually occurs at the voltage v, while $(i_o)_4$, $(i_o)_5$, etc., giving "sparks" for which $R_s i_o$ is less than 300, all cut the characteristic at voltages likewise much less than 300, that is, $R_s i_o$ is neither the atmospheric breakdown voltage nor the voltage at which the discharge occurs.

As will be seen in the next section, this interpretation is borne out when means are found to separate the two kinds of discharge.

Further evidence as to the different nature of the "spark" occurring below and above the break point is given by a study of the spectrum of the discharge. For this study, spectrograms were made, by means of a quartz spectrograph, of the light from extremely small, just visible, sparks, in both current ranges. With

PLATE I.



Spectrograms of arcs, glow discharges, break arcs and break sparks with gold and platinum electrodes.

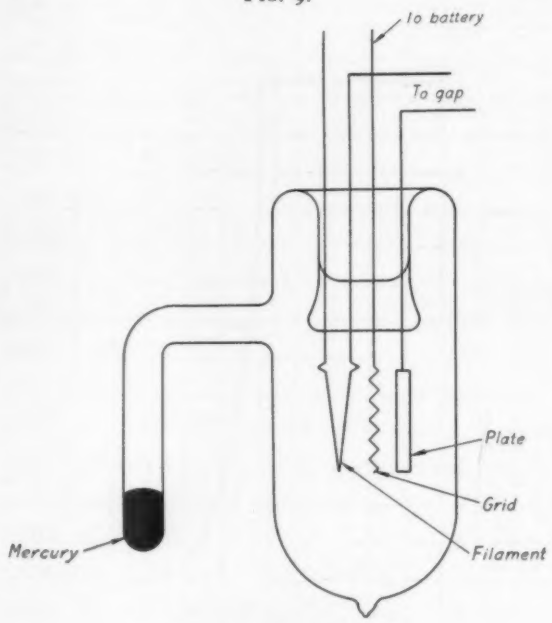
these small sparks it was necessary to photograph the integral light of many thousands of discharges, for which purpose the contact device shown in Fig. 6 was operated by a commutator running for twenty-four hours or more.

Spectrograms were obtained in this way for the spark with separating gold and platinum electrodes. Then with the same apparatus, spectrograms were taken of the ordinary arc spectra of the same elements, and of the glow discharge which passes between stationary electrodes at currents too low for the true arc, and at voltages of 300 or over. Inspection of these spectrograms, which are reproduced in Plate I, shows clearly that, judged by the character of the spectra:

(1) The discharge below the "break point" is identical in character for both (and inferentially for all) electrode materials, and is also identical with the glow discharge.

(2) The discharge above the "break point" is different for the two (and inferentially for all) electrode materials, and is identical in each case with the arc characteristic of the materials.[2]

FIG. 9.



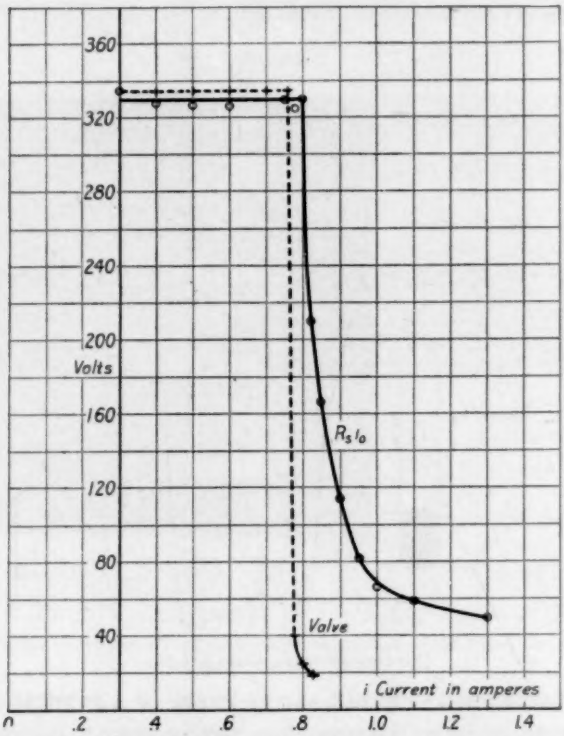
Hot filament mercury-vapor valve.

THE ISOLATION OF THE BREAK ARC BY MEANS OF A SHUNTED VALVE.

It is evident from the preceding section that it is not possible by the methods which have been outlined to carry the arc characteristic to very low-current values, because of the interposition of the glow discharge when the electromotive force rises above 300. In order to isolate the break arc from the break spark, recourse was made to a hot filament mercury-vapor valve shown diagrammatically in Fig. 9. This valve has a breakdown voltage which may be varied by varying the voltage applied to the grid, over a range from fifteen to twenty up to several hundred volts, depending on construction, vapor-pressure, etc. This valve was used entirely as an accessory to the shunted resistance method of

obtaining the break arc characteristics. Its manner of functioning is shown clearly by the data of Fig. 14, where the top curve to the left is the previously discussed $R_s i_0$ curve characteristic for air. When the valve is also placed in shunt and set by means of the appropriate grid voltage to break down at some value well

FIG. 10.

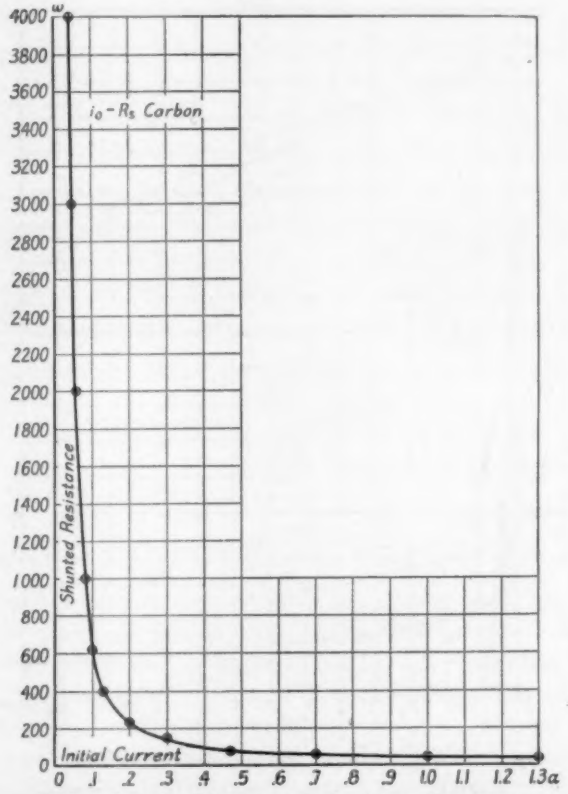


Breakdown voltages as determined by hot filament valve compared with terminal voltages.

below 300 volts, for instance 200 volts, the entire arm of the curve for currents below the break point disappears, the true spark now taking place through the valve, making it thus possible in observing the opening contact to restrict our observation entirely to the break arc. With the valve in action, the shunted resistance curve (right-hand curve, Fig. 14) is a continuation of the break arc arm of the curve to lower current values and higher shunted resistances than are possible as long as the air spark is free to occur at the contacts.

The mercury-vapor valve makes it possible to test the interpretation of the break arc characteristic given in the last section, by setting the grid voltage so that the valve just prevents the spark which has just been made visible by any given shunted resistance. It is then possible from a separate static calibration

FIG. 11.

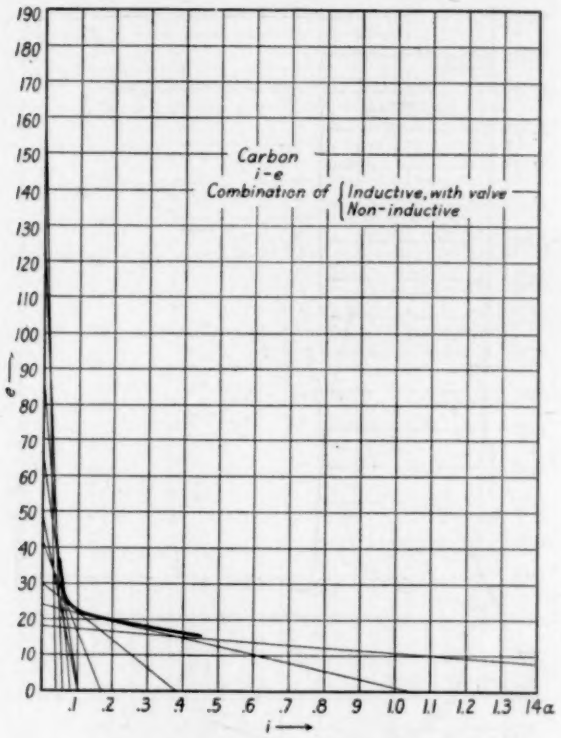


Critical-shunted-resistance-*versus*-current curve for carbon.

of the valve to determine what is the voltage of the discharge. Fig. 10 shows the result of such an experiment on platinum electrodes. Here the abscissæ are initial currents, the ordinates, the product $R_s i_0$, or valve breakdown voltages. At low current values, the product $R_s i_0$ is approximately 300 as before explained. For currents above the break point the product $R_s i_0$ decreases uniformly in value. However, upon using the valve to determine

the actual breakdown voltages, it is found that while for currents below the break point, the breakdown voltage is close to 300, it falls suddenly to about 50 near the break point while the value of the product $R_e i_0$ merely begins to decrease gradually; beyond this sudden drop the breakdown voltage decreases slowly, always

FIG. 12.



Minimal length arc characteristic for carbon.

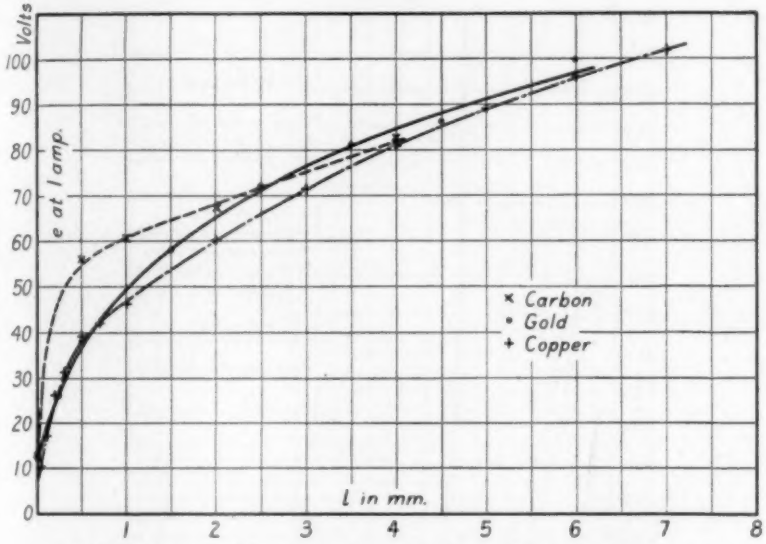
remaining well below the value of the product. The close similarity of the experimental data with the curves of Fig. 8 serves to confirm the theory used.

EXPERIMENTAL DETERMINATION OF ARC CHARACTERISTICS.

The method of determining what we shall call *minimal length arc characteristics* which has just been described has been applied to a number of substances under a variety of conditions. The materials to which chief attention has been given are carbon,

platinum and gold; for these, very complete data have been obtained. Other materials, *e.g.*, copper and iron, have been utilized to illustrate points of interest, but, for reasons which will appear later, their characteristics have not been so completely determined. In general, the characteristics have been determined

FIG. 13.



Voltage *versus* arc length data at 1 ampere for carbon, gold and copper.

in an inductive circuit with shunted resistance, observation being made both with and without the valve; but for the low-voltage high-current conditions, observations have also been made by the use of a non-inductive circuit. These methods should, as has been shown, lead to identical results when the series of tangents are drawn between the final voltage and the broken current. Such, in fact, is found to be the case, so that the characteristic curves shown are usually built up from observations by both methods.

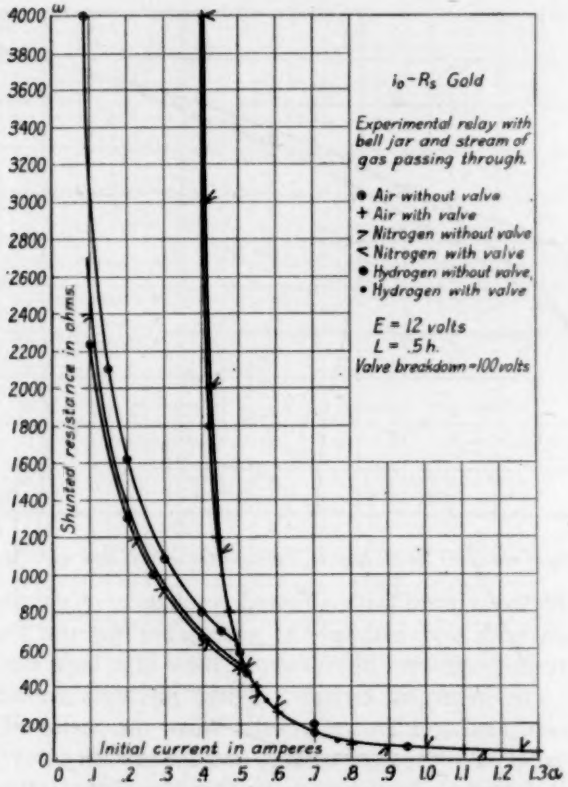
In the following paragraphs brief descriptions will be given of the characteristics as shown in the accompanying figures.

Carbon.—The minimal length arc characteristic of carbon as obtained from its critical shunted resistance, and by measurements with a non-inductive circuit, is shown in Figs. 11 and 12. The position of this characteristic in reference to the finite length characteristics is indicated by the dashed line in Fig. 1. In Fig. 13

is shown the voltage-*versus*-length relation for a current value of one ampere.

The most significant thing to notice about the carbon minimal length characteristic is that it does not exhibit the discontinuity from arc to glow which the metals display. This behavior is

FIG. 14.

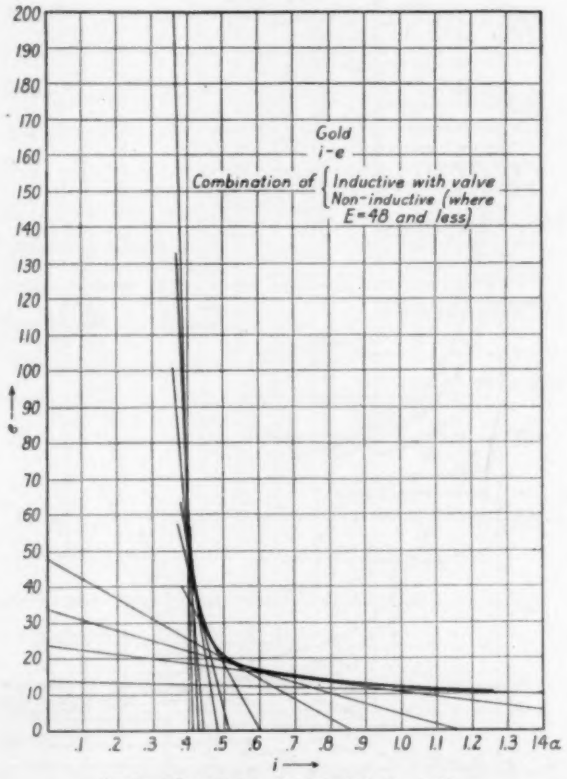


Critical-shunted-resistance-*versus*-current curve for gold.

also a feature of the finite length characteristics. In the critical-shunted-resistance-*versus*-initial-current plot (Fig. 11) this behavior is reflected in the absence of a "break point," and the failure of the shunted valve to alter the curves in any way. As to the position of the minimal length characteristic on the characteristics diagram, its considerable separation from the first easily measurable finite length characteristic (.5 millimetre) is notice-

able. This is also shown by the voltage-*versus*-length plot of Fig. 13. In this figure, the 4, 3, 2, 1 and ½ minimal voltages lie along a very good straight line, which extrapolated would indicate a zero length voltage of over 50 instead of the 13 actually found. This is in marked distinction to the similar data for gold

FIG. 15.



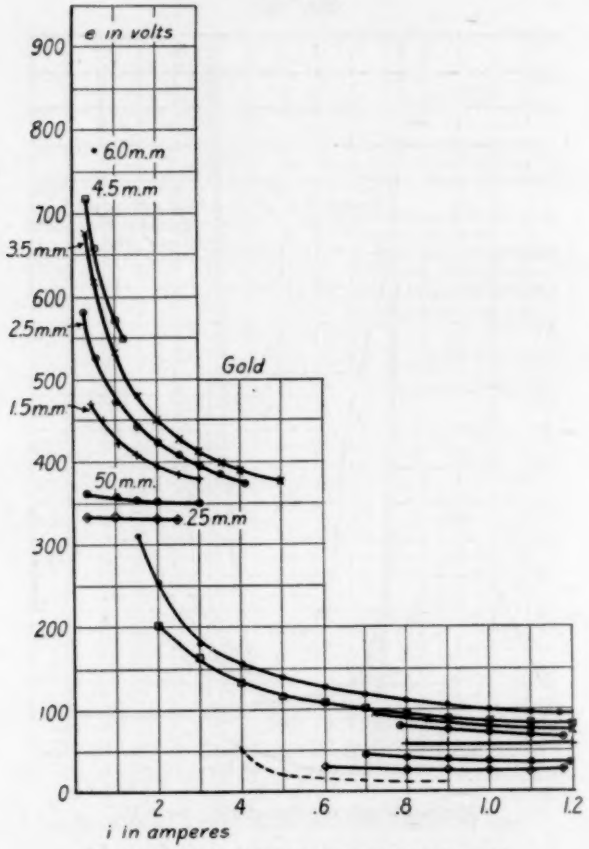
Minimal length arc characteristic for gold.

shown in the same sheet, where the corresponding points form a smooth curve on which the minimal length value fits without apparent discontinuity. Data for copper, from a separate investigation,[1] shown on the same figure, exhibit a behavior similar to that of gold.

Gold.—Figs. 14 and 15 show the results for gold electrodes, and in Fig. 16 is plotted as a dashed line the minimal length

characteristic to the same coördinates and scale as the finite length characteristics, the latter determined specially for this study from 8-mm. diameter electrodes. The outstanding feature of the gold minimal length characteristic is the occurrence of a *limiting value*

FIG. 16.



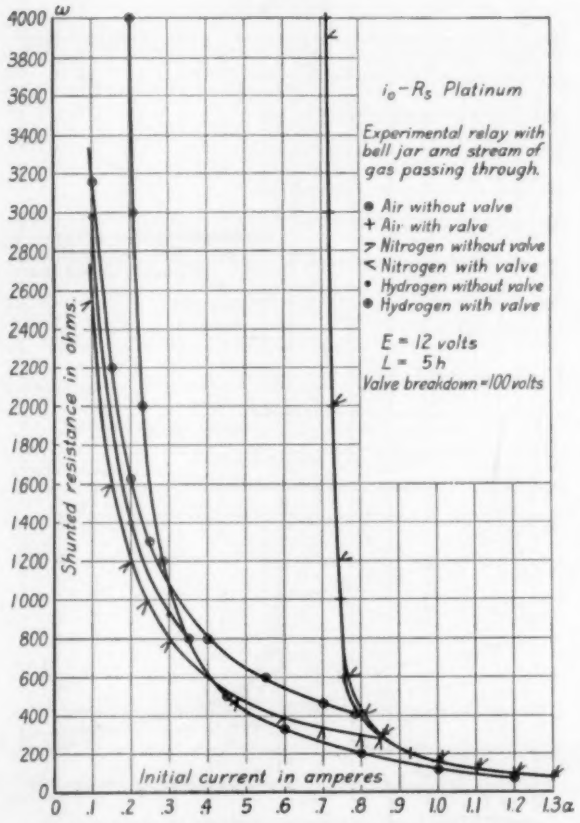
Finite and minimal length characteristics for gold.

to the current, namely, .4 ampere, corresponding to 50 volts, below which point the discharge occurs (in air) at a voltage of 300. This limiting current is, as Fig. 16 shows, a feature as well of the finite length characteristics. *Both in respect to the value of the limiting current, and in respect to the minimum value of the voltage, in the voltage-length relations* (Fig. 13) *the minimal*

length characteristic in the case of gold is obviously a member of the family of finite length characteristics, closely taking the position that a simple extrapolation of these would indicate.

Platinum.—The critical shunted resistance curve for platinum (Fig. 17) is similar to that for gold in showing a sharp break

FIG. 17.



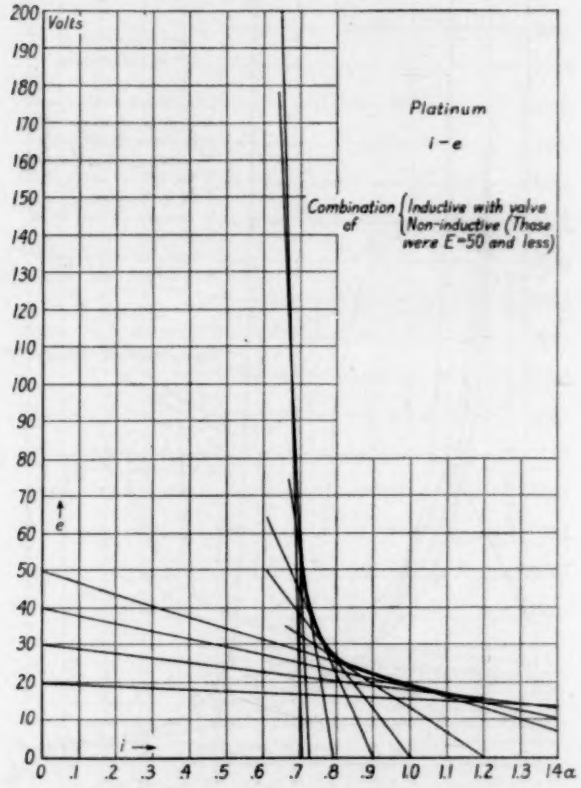
Critical-shunted-resistance-*versus*-current curve for platinum.

point. This break point is, however, shifted from .5 ampere to .8 ampere and the corresponding arc characteristic has a limiting value of .7 ampere instead of .4 ampere. This higher value of the limiting current is a feature also of the finite length arcs, a few of which are shown in Fig. 19, on which the minimal length characteristic is shown as a dashed line. The experimental difficulties

of obtaining platinum arc characteristics are very great because of the tendency of the electrodes to melt immediately a true arc forms; those shown are, however, sufficient to prove that the family resemblance between the finite and minimal length characteristics shown by gold also holds here.

Other Metals.—Critical shunted resistance curves are shown

FIG. 18.

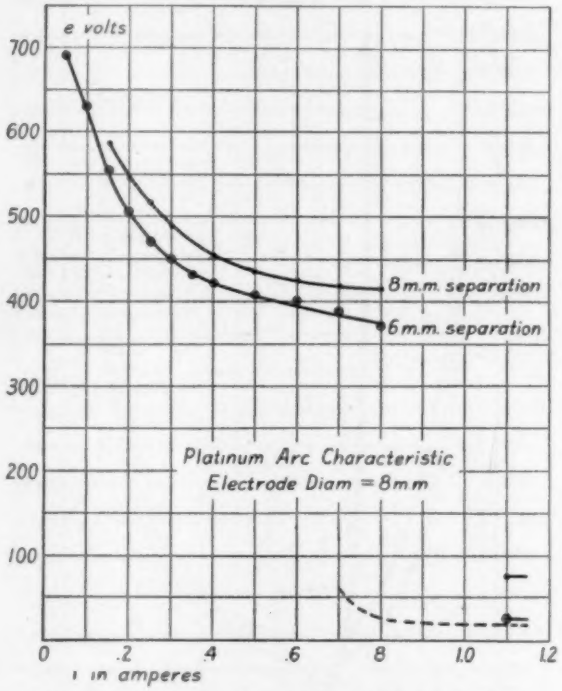


Minimal length arc characteristic for platinum.

for silver, iron and copper (Figs. 20, 21 and 22). These all show the break point characteristic of the transition from arc to spark discharge. The position of the break point varies with the material and, as will be discussed later, with the oxidation or other surface conditions. Because of this variability and also in part because of the minor importance of these materials as relay contact

metals, observations sufficient to establish their complete minimal length arc characteristics were not attempted. A large number of materials were studied only sufficiently to establish the position of their break points. No other material has been found which gives as high a break point as platinum and no clean metal breaks

FIG. 19.



Finite and minimal length arc characteristics for platinum.

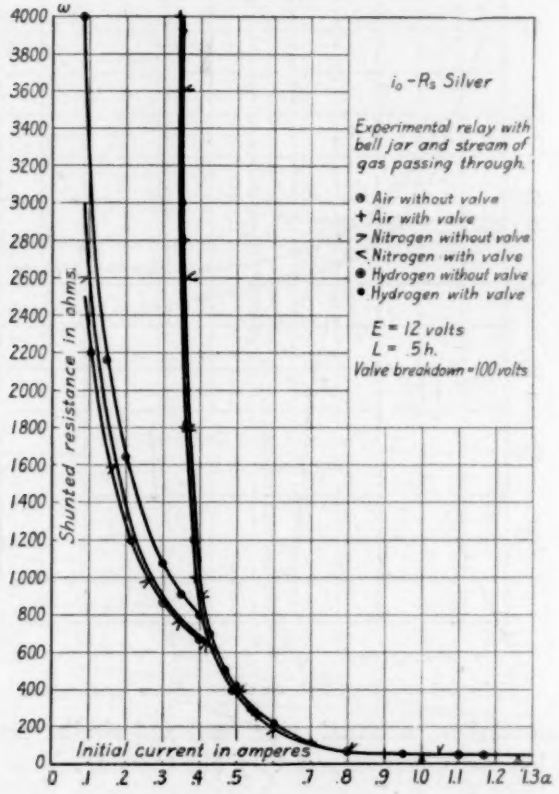
lower than carbon, although zinc, lead and similar metals when oxidized behave in this respect very like carbon.

ANODE AND CATHODE OF DIFFERENT MATERIALS.

Measurements were made of the phenomena at contact pieces of two different metals. The derived minimal length arc characteristics for gold *versus* platinum and for carbon *versus* platinum are shown in Figs. 23 and 24. In general, the result is that if the anode metal is the one of lower voltage-current characteristic, the characteristic of the unsymmetrical pair is that of the anode.

If, on the other hand, the anode material has the higher arc characteristic the compound characteristic is shifted toward the characteristic of the anode, but is not identical with it. In other words, if the anode characteristic is the upper one, the compound characteristic will try to move to the upper value, but in the presence of the other metal can only do this to a partial degree.

FIG. 20.



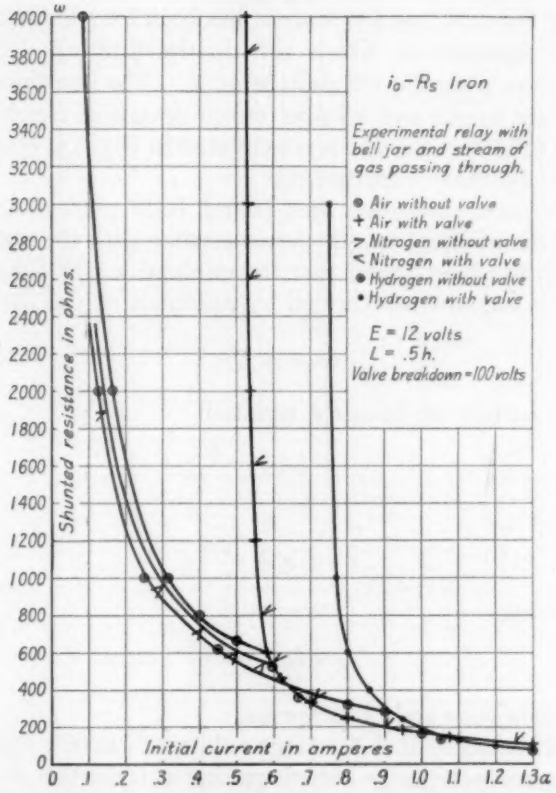
Critical-shunted-resistance-*versus*-current curves for silver.

PHENOMENA IN VARIOUS GASES.

In addition to the shunted resistance characteristics, taken in air, we have a number of observations in nitrogen and hydrogen. These are shown on the same figures as the air characteristics. The breakdown voltages of these gases are somewhat lower than that for air, consequently the low current branches of the critical-shunted-resistance-*versus*-current curves are lower. In the case of

nitrogen this is practically the only difference in the complete curves, that is, the arc characteristics are unaffected. In the case of hydrogen we note some effect on the arc characteristic. Thus iron in hydrogen continues to give the true spark up to considerably higher values of current than in air. Conversely the break point

FIG. 21.



Critical-shunted-resistance-*versus*-current curves for iron.

of platinum is at a considerably lower current in hydrogen than in air.

DISCUSSION.

It is of interest to study in what respect these minimal length arc characteristics are similar to, and in what respect they are different from, the characteristics yielded by the ordinary method of studying arcs with finite separation of the electrodes.

First of all, the minimal length characteristics are similar in

general appearance to the usual characteristics, that is, they are approximately hyperbolic curves. They cannot, it is found, be represented by the simple equation $e = \alpha + \frac{\gamma}{i^n}$, because in all cases the increase in voltage, as the limiting current is approached, is more rapid than any values of the constants in this equation can handle. This, however, is not to be considered evidence that the discharge is not a true arc, since it has been long known [3] that the complete equation of which this is the limiting case when l becomes zero is invalid for short lengths. The non-linear relation between arc length and voltage, which deviation from this equation also involves and which is exhibited in Fig. 13, is abundantly supported by other experiments.

While no equation has been found in the present study which will link the minimal length characteristics with the arcs of finite lengths, it has been found that the minimal length characteristics themselves are well represented by equations of the form

$$e = \alpha + \frac{\gamma}{i - c}.$$

Thus for carbon we have the equation

$$e = 15.5 + \frac{.6}{i - .02}$$

for gold,

$$e = 11.5 + \frac{1.0}{i - .38}$$

for platinum,

$$e = 15 + \frac{1.35}{i - .67}$$

where e is in volts and i in amperes.

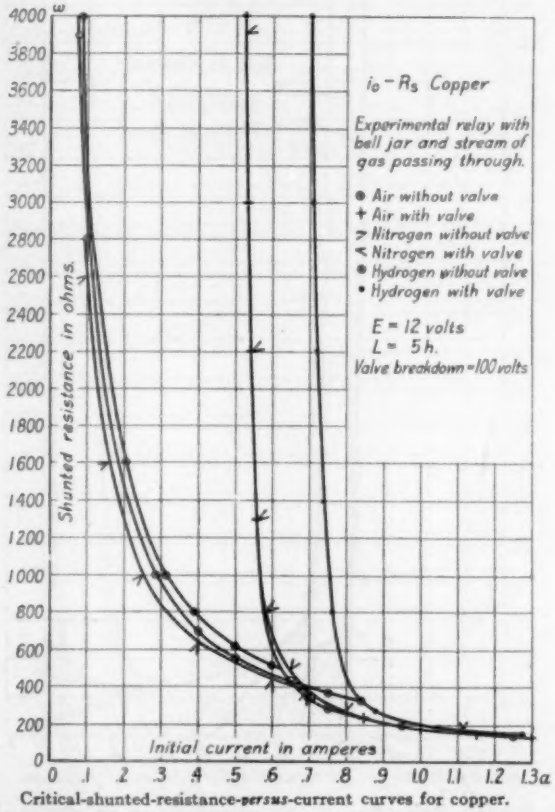
It will be noted that for large values of current these expressions become practically indistinguishable from the ordinary arc equation with exponent unity.

In the case of the metals, the minimal length characteristics are very strikingly identified with the family of finite length characteristics by the *occurrence of lower limiting current values,* as is illustrated very clearly by the gold arc characteristics of Fig. 16, which, instead of extending indefinitely towards zero current, are sharply terminated. These lower limiting values of current have been discussed at length by Stark [4] and by Malcolm.[5] From the

experiments of the former, the following set of values for an electrode separation of 1.8 mm. are selected as of special interest.

	Electrode Material.				
	C	Cu	Al	Fe	Pt
Limiting Current in Amperes	.013	.45	.57	.73	1.5

FIG. 22.

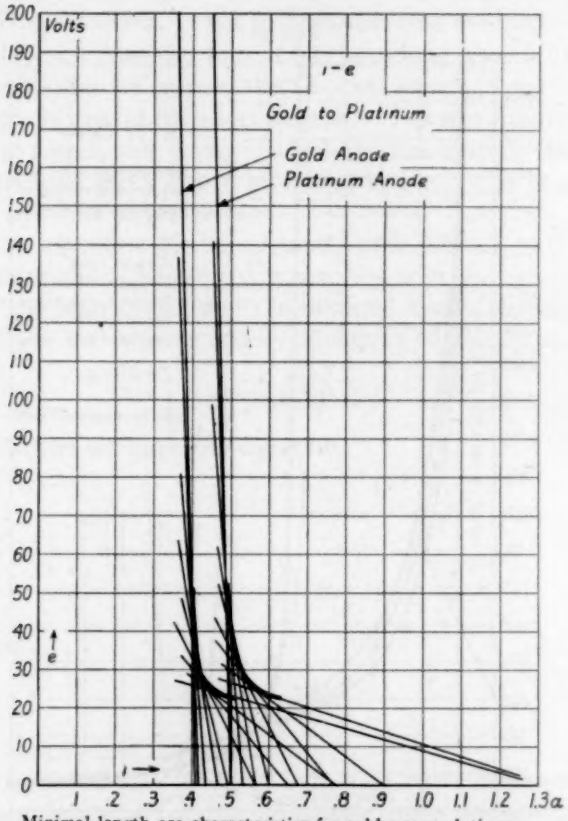

Shunted resistance in ohms.
Initial current in amperes
$i_0 - R_s$ Copper
Experimental relay with bell jar and stream of gas passing through.
Air without valve
Air with valve
Nitrogen without valve
Nitrogen with valve
Hydrogen without valve
Hydrogen with valve
E = 12 volts
L = 5 h.
Valve breakdown = 100 volts

Critical-shunted-resistance-*versus*-current curves for copper.

This order agrees with ours in that carbon shows the lowest value, platinum the highest, copper and iron intermediate values, although the latter are placed farther apart than the data here shown indicate, a difference of small significance considering the different order of electrode separation and also the oxidizable nature of these materials, which influences the results to a marked degree. Malcolm notes that the transition from glow to arc

takes place at a current value which is higher the higher the melting point of the metal, and the less oxidizable the metal is, which is in general the case for the limiting currents observed in the present study.

FIG. 23.

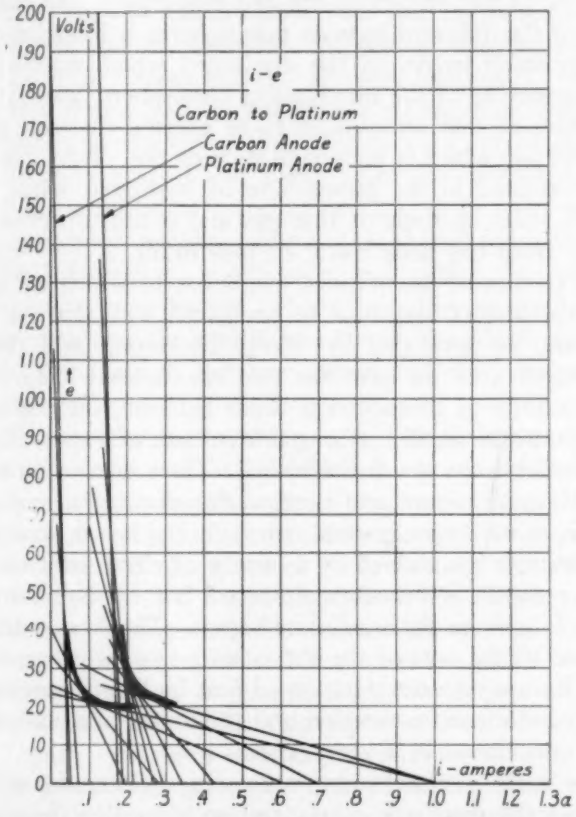


Minimal length arc characteristics for gold *versus* platinum.

Dependence of the break arc phenomena on the oxidation or other abnormal condition of the surface may naturally be expected to be greater than is the dependence of the finite arc characteristics noted by Malcolm. Where, for instance, a stably burning arc may clean off the electrode surfaces, the break arc always starts from the surface as it exists in the cold condition after exposure to the atmosphere. The break arc phenomena are in fact found to be greatly dependent on the surface conditions of the elec-

trodes. The "break point" is thus very constant with gold, which is comparatively non-oxidizable, but much less definite with iron, copper, silver and other oxidizable metals. Even platinum exhibits some wandering of this point; these variations are

FIG. 24.



Minimal length arc characteristics for carbon *versus* platinum.

not, however, of such magnitude as to invalidate the general parallelism between the order of the limiting currents for finite and minimal length arcs.

Turning now to the behavior of opening contacts consisting of two dissimilar materials, the predominant effect of the anode is an agreement with what has been previously found in the study of the arc, for instance, by Stark,[4] and recently by Nottingham.[1]

That the anode characteristic does not entirely prevail when the cathode material is the one of lower voltage-current characteristic appears to be not unreasonable. It is probable that the discharges with which we are here concerned occur while the electrodes are still appreciably in contact so that the discharge must be through a mixture of the vapors of the two materials. The rather small effects of the different gaseous atmospheres is likewise consistent with the small length of the discharge, which does not permit much admixture of the surrounding atmosphere, leaving the principal effect of that atmosphere to be exerted through the nature of the surface which is formed in its presence. Iron, for instance, is not oxidized in the atmosphere of hydrogen while platinum probably takes up some of that gas and is thus different in composition from the same metal surface in air.

The picture of the minimal length arc to which we are led by these experiments may now be compared with that of the finite length arc, as developed by Stark, Thomson,[7] and others. In finite length arcs we have the two electrodes widely separated, with a column of incandescent vapor between, the vapor coming chiefly from the anode. Along this column of vapor three different potential drops are distinguished: The anode fall, the cathode fall, both quite abrupt and close to the electrodes, and the drop, which is much more gradual, through the space between these. The current is maintained by a supply of electrons from an area on the cathode, which is maintained hot by bombardment of positive ions from the anode and vapor. The size of the current is decided by the area of the hot cathode spot, which results from an equilibrium between the gain of heat by bombardment and the loss by conduction, convection and radiation, in a manner which is only understood in a very general way.

Now in the minimal length arc we have electrodes still in contact when the discharge starts and so at nearly the same temperature. The vapor present will be from both electrodes, although predominantly from the material of lower vaporizing temperature. Anode and cathode fall will not have sufficient space to develop independently and so will overlap. The equilibrium condition which determines the voltage-current relation may, therefore, be expected to be materially altered from that holding with wide separations of the electrodes. The minimal length arc characteristics may, however, be expected to merge

fairly uniformly into the wide separation characteristics as the electrode distance is increased, except where initial surface conditions greatly modify the initiation of the discharge, in which case the transition from minimal length to long characteristic might be more or less discontinuous.

Attention may be called to the fact that the minimal length characteristics, and in particular the critical shunted resistance curves with their " break points " are only obtained as shown in the diagrams *if the contacts are broken cleanly and sharply.* If the electrodes separate with a sliding motion the curves are moved in toward the origin, and the break point goes to lower current values. This behavior of a sliding break is to be ascribed to the generation, through friction, of heat other than that which the discharge itself furnishes, a condition not unlike that presented by the use of an incandescent cathode heated by an auxiliary current. For such arcs the equilibrium conditions which control the size of the hot cathode spot are altered and the voltage-current relation changed.

It will be noticed that nothing is said in the conception here presented about the process by which the arc is ignited. It is simply assumed that when the voltage-current conditions are those pertaining to a stable arc, the contact pieces have become hot enough by virtue of the previous Joule heating for thermionic emission which starts off the process whose equilibrium condition is the stable arc. It is conceivable that conditions might be found, such as very rapid separation of the electrodes, which would not allow sufficient heating to permit the ignition process to take place. It is also conceivable that under certain conditions the smallest " spark " observed would be merely a minute incandescent spot due to Joule heating, no arc being formed. These possibilities have not, however, been realized in the present experiments. No dependence whatever of the break arc phenomena on velocity of contact separation has been found, even at velocities up to 60 centimetres per second. Spectroscopic study of the smallest visible sparks, as already described, shows them to be fully developed arcs.

All the evidence, together, appears amply to justify the view that the discharge occurring between separating electrodes, when the current broken is greater than a certain critical value characteristic of the electrode material, is a true arc, and that a " zero "

or minimal length characteristic is a true member of the family of arc characteristics.[7]

THE COMPLETE VOLTAGE-CURRENT CHARACTERISTICS OF THE DISCHARGE BETWEEN SEPARATING CONTACTS.

The phenomena which have been described and measured in this paper make it possible to describe with a definiteness hitherto not realized, the voltage current characteristics of those discharges which occur upon the breaking of simple electrical circuits. Heretofore, the chief treatments of such discharges have been confined to the sparks occurring under such conditions that the atmospheric breakdown voltage is alone in question. Günther,[8] from a study of oscillograms, developed the following empirical equation for the discharge between opening electrodes in an inductive circuit:

$$i = i_o - a_o t$$

where

$$a_o = A - \frac{B}{E} + \frac{Ci_o}{EL}$$

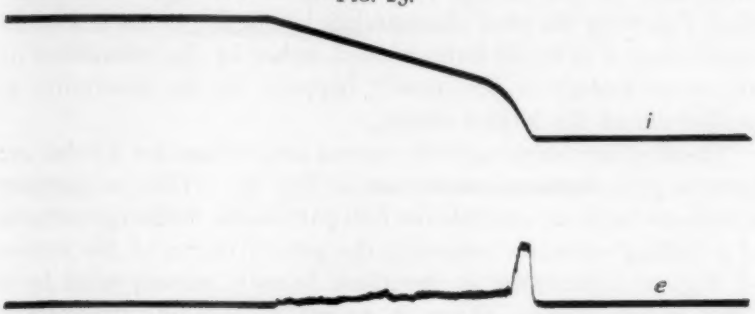
where A, B and C are constants, i_o and E have the significance used in this paper, L is the inductance of the circuit, and t is time. The subject-matter of this paper may be used to obtain an equation which is based on the minimal length arc characteristic and is, therefore, to a much less degree empirical than is the expression of Günther.

According to the line of thought of this paper what occurs when electrodes in a simple non-inductive circuit are opened is first of all an abrupt drop in the current value, which may or may not be interrupted by an arc, dependent on whether or not the minimal length arc characteristic is cut. If the electromotive force is sufficiently high this characteristic will be cut and an arc will be formed, the duration of which will depend upon the speed of separation of the electrodes and upon the electromotive force.[9] The nature of such non-inductive arcs is well illustrated by the oscillogram, Fig. 3.

Technically, probably the much more important case is the one in which there is inductance in series with the contact. In this case, immediately upon the contacts starting to open, the voltage will rise and the zero length arc characteristic will be cut at once. From this point on, as the contacts open, the current will decrease, the discharge running first along the zero length arc characteristic

and then moving to characteristics of continually increasing length until the arc breaks off. The manner in which the arc is broken

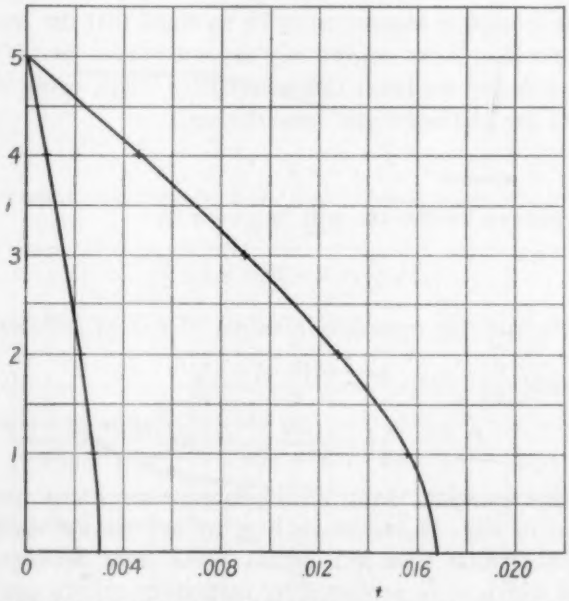
FIG. 25.



Oscillograms of voltage and current at the break of an inductive circuit; gold electrodes.

will differ according to the material. Thus with carbon the arc characteristics will be followed down to extremely small currents;

FIG. 26.



Calculated-current-*versus*-time curves for the discharge on breaking an inductive circuit with carbon electrodes.

on the other hand, with a metal such as gold, the arc characteristics will be followed until the limiting current value is reached, after

which the voltage will rise to some higher value, which in the absence of any metal vapor will be the air spark or glow value. From here on, the voltage may be expected to again rise somewhat, following the glow characteristic of the air, or air and metal vapor, until it is finally extinguished, either by the exhaustion of the stored energy or, as usually happens, by its absorption in oscillations of the broken circuit.

Oscillograms showing both current and voltage for a break arc between gold electrodes are shown in Fig. 25. Here, in complete agreement with our analysis the first part of the discharge consists of a falling current (following the general form of the curves of Fig. 26, calculated as described below), accompanied by a slowly rising voltage. When, however, the limiting current value is reached, the voltage immediately leaps to a high value (ca 300), the current falling henceforth at a different rate.

The course of an inductive discharge with time when this follows the arc characteristics may be simply calculated if we assume the complete separation to be so small that the zero length arc characteristic is not appreciably departed from, and if we have an expression for the latter characteristic. Thus, using the minimal length arc characteristic here derived,

$$e = \alpha + \frac{\gamma}{i - c}.$$

The life history of the arc will be given by

$$-L\frac{di}{dt} + E - Ri = \alpha + \frac{\gamma}{i - c}.$$

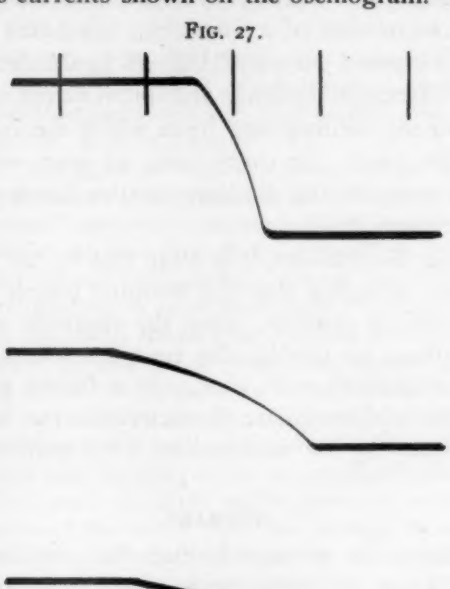
The solution of this equation in terms of t is as follows:

$$t = \frac{L}{2R}\log\left(\frac{R}{L}[i-c]^2 - \frac{[\alpha - E][i-c] + \gamma}{L}\right) - \frac{\gamma}{2R}\left(\frac{2L}{\sqrt{\alpha^2 + 4R\alpha}}\arctan\frac{(2R[i-c] - \alpha + E)}{\sqrt{\alpha^2 + 4R\alpha}}\right).$$

Plots of this equation, using appropriate arc constants for carbon, are shown in Fig. 26, while in Fig. 27 are shown oscillograms of current against time for actual break arcs between carbon electrodes which were protected by insulating collars and allowed to separate only a minute distance. The oscillograms are seen to have the general character predicted by the above equation. The course of voltage with time is to be obtained immediately by

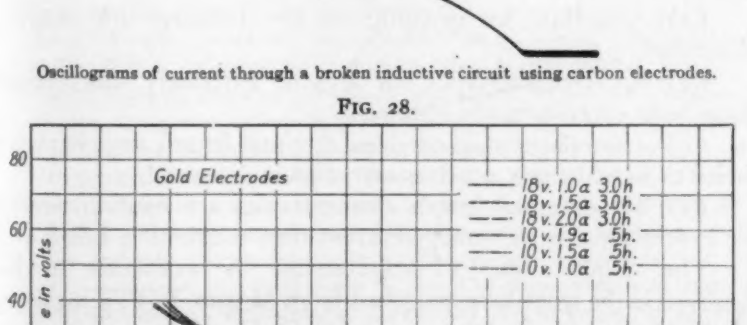
reading from the arc characteristic curve the voltages corresponding to various currents shown on the oscillogram.

FIG. 27.



Oscillograms of current through a broken inductive circuit using carbon electrodes.

FIG. 28.



Voltage-current characteristic as read off oscillograms of discharges between gold electrodes, using various values of initial current and inductance.

If this explanation of the break "spark" is correct, the voltage-current relation, as read off from oscillograms of both current

and voltage, should be independent of the inductance or the magnitude of the current broken (provided this is above the limiting value for the occurrence of a true arc). That this is so is shown by the voltage-current curves of Fig. 28 (gold electrodes) where a variety of different inductances and initial values of current were used to obtain the oscillograms from which the voltage and current values are read. In every case, as soon as the electrode separation is complete the discharge settles down upon the same characteristic curve.[10]

From these illustrations, it is clear that by the use of the arc characteristics, including that for minimal length as here determined, it should be possible, given the electrode separation as a function of time, to predict the complete trend of the break discharge characteristic with time. In a future paper it will be shown how minimal length arc characteristics can be used to solve typical problems in the elimination of "sparking" at opening contacts.

SUMMARY.

(1) Evidence is presented that the discharge occurring between separating electrodes is, for large currents, an arc; for small currents, an atmospheric spark.

(2) A method for isolating the arc discharge for study is described.

(3) Arc characteristics for arcs of extremely short length have been experimentally obtained.

(4) The relationship of these minimal length arc characteristics to finite length arc characteristics is discussed.

(5) The minimal length characteristics are used to develop an expression for the voltage-current-time relations in break arcs.

The writer wishes to acknowledge the assistance he has received in the work here described from Messrs. E. F. Kingsbury, K. K. Darrow, A. L. Johnsrud and S. D. Morrison.

NEW YORK,
April 18, 1924.

NOTES.

[1] Nottingham: *Trans. Am. Inst. E. E.*, **42**, 12–19 (1923).

[2] Differences in the general appearance of the spectrograms are caused by unavoidable differences in exposure and alignment of apparatus. The conclusions just drawn are based on study of the positions of the emission lines. In a very few cases there are variations in the distribution of

intensity of the lines which probably constitute real differences between the arc and break arc, or the glow and the break spark. These are, however, so rare as not to seriously affect the validity of the general conclusions.

[3] Duddell: *Phil. Trans.*, **203**, 338 (1904).

[4] Stark: *Ann. d. Physik.*, **12**, 692–699 (1907); also paper by Cady and Arnold (*Phys. Zeit.*, **24**, 890–906, 1907) where transition points from arc to glow are observed agreeing well with Stark's values here tabulated.

[5] Malcolm: *Phys. Zeit.*, **8**, 471–481 (1907).

[6] J. J. Thomson: "Conduction of Electricity through Gases," 2d Ed., p. 613.

[7] It may be pointed out that, strictly speaking, the envelope curve which is here called the minimal length arc characteristic, may be merely a simple graphic way of describing certain critical discharge conditions. While it is here considered that this curve is actually a minimal length arc characteristic, which is of the same nature as the finite length characteristics, and is governed by generally similar conditions of electrical and thermal equilibrium, the experimental findings of the paper, as embodied in it, would be unaffected by other conceivable views of the nature of the break arc. Thus it might be possible to interpret this envelope curve as depending on the attainment of certain thermal conditions during the process of opening. If such were the case, the curve in question would still describe the critical arcing conditions and could still be used to determine conditions for avoiding the formation of the arc. It would not, however, be expected to show any consistent relation with the finite length arc characteristics, such as the similar location of the lower limiting current.

[8] Günther: *Ann. d. Physik.*, (4) **42**, 94, 1913.

[9] This is also the picture of the phenomenon as conceived by Philippi ("Uber Ausschaltungsvorgänge und Magnetische Funkenleschung," Berlin, 1910), and by Krauss (*Electrotechnick Maschinenbau*, **31**, 712 and 744, 1913).

[10] In taking these oscillograms the voltage was tapped off part of a resistance of several megohms and raised to measurable value by the use of a vacuum tube amplifier, in order not to alter the nature of the discharge by the introduction of a shunt circuit. The electrodes had protecting collars of glass, formed by fusing glass beads on the rods, which were then filed off so as to expose as short a length as possible. The presence of the glass probably altered the discharge characteristic appreciably, and the curves are to be considered solely in regard to the immediate question at issue, namely, the independence of the characteristic of inductance or initial current value.

The Paper Supply.—The United States is in many lines the most extensive consumer of products of the soil and mine, and is also among the most abundant producers. Consumption, however, is outrunning production in some highly important industries, and a dangerous indifference to the situation is exhibited by most of our people. Our oil supplies, for instance, are no longer sufficient for

our needs, and these needs will be immensely increased in the near future. Sugar, of which we are the largest user, has long been most largely imported.

A pamphlet has just been issued under the auspices of the U. S. Department of Agriculture (Dept. Bull. 1241) in which an extended statement is given as to the critical situation in the supply of wood-paper stock. The use of wood as a raw material for a merchantable pulp dates from a little over fifty years ago, when the method of treating wood with sodium hydroxide solution at a temperature of about 300° F. was perfected. This cheapened greatly the supply of paper for general purposes. Later, other methods were invented, one of the most important being the use of sulphites instead of alkali. Much greater employment of wood was brought about by the introduction of ground work, produced merely by direct mechanical methods. Such material is not usable alone, as it has no adhering quality. It is mixed with a small amount of true pulp. Such mixtures are now largely used for newspapers, and have resulted in the production of paper that decays very rapidly, so that newspapers a few years old crumble readily. The liability to this decay is a very serious matter.

In 1922, the American public consumed more than eight million tons of paper, more than all the other countries of the world combined. A very considerable amount of waste paper was re-worked, constituting an important item of supply. Many attempts have been made to use waste paper, but until lately the difficulty of removing the ink has been a bar to success. This problem has been solved in a measure, but the collection of waste paper involves an item of cost that prevents extensive use. Obviously, the collection of large amounts of waste paper can at present only be carried on economically in communities, but a double purpose will be served by developing this industry, for not only will an important supply be added to our resources, but the litter of the streets will be diminished.

At present the United States is importing a large proportion of its paper-making materials. Naturally a great deal comes from Canada, but restriction of exportation from there is threatened. It is important that the United States should be able to secure the raw materials for all important manufactures within its own borders. Conservation, therefore, of such natural resources as coal and oil, which cannot be reproduced at will, should be promoted. As regards paper supply, the most important point is the reforesting of suitable areas. The experts of the Forest Service of the Department of Agriculture have been giving close attention to the question, in consequence of the action of the American Paper and Pulp Association. The report, from which the data here presented are taken, refers to the importance of reforestation, which is not only feasible but is essential if the country is to be independent of foreign supplies.

H. L.

DO GREEN PLANTS HAVE THE POWER OF FIXING ELEMENTARY NITROGEN FROM THE ATMOSPHERE?*

BY

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FOR more than half a century, scientific men, taken by and large, have regarded as settled in the negative the question of whether or not green plants *without the aid of bacteria* possess the power of fixing elementary nitrogen from the atmosphere. The evidence adduced by Boussingault [1] and by Lawes, Gilbert, and Pugh,[2] was assumed to be final proof in support of the attitude to which we have just referred. In more recent years, however, and specially since 1905, a number of authors and experimenters have advanced the view that the contentions of Ville,[3] a contemporary of Lawes, Gilbert, and Pugh, to the effect that green plants possess the power of fixing atmospheric nitrogen in the form of the element could not be waved aside without further careful study. Moreover, those authors have furnished evidence, some of which was convincing and some not quite so, in support of the idea that green plants do possess the power of fixing nitrogen from the free nitrogen of the air. We shall attempt below to make a critical examination of the situation which is thus created by a reawakened controversy. We desire first, however, to present evidence which we have obtained during the past year, which seems to us to give greater strength to the assertion that some green plants do possess the power of fixing free nitrogen from the air, and perhaps even disposing finally of that question. In the investigations to which we have referred as being reported since 1905, we have had successively the work of Jamieson,[4] Mameli and Pollacci,[5] Moore, Webster and Whitley,[6] and Wann.[7] These experimenters, working with various plants and by various methods, have all come to the same general conclusion. It is our

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purpose to defer the discussion of the weak and strong points of each of these researches until we have reached that part of this paper which deals with the critical study promised above.

THE PLAN AND METHOD OF OUR EXPERIMENT.

Our experimental procedure was essentially that of the ordinary solution culture. Both wheat and barley plants were studied in an extensive way. Other plants like *Bromus, Pinus,* and *Pisum,* were studied in a much more limited way. In the case of wheat, a number of different experiments were conducted, the growth period allowed the plants varying in different tests from seven weeks to fourteen weeks. In the case of barley and wheat, except as otherwise noted, five plants per culture jar were grown. In some cases one-quart Mason jars were employed and in others two-quart Mason jars. All experiments were conducted in a greenhouse and in the open air thereof. In one experiment with wheat, as will be indicated below, the culture jars were kept under a bell-jar and in an atmosphere freed from ammonia, nitrous acid and nitric acid. In the large series with wheat and in that with barley, different sub-series received different treatments as regards the supply of nitrogen, one sub-series receiving no nitrogen except that in the seed and the traces in the chemicals used, others receiving different fractions of the full amount of nitrate used in a modified Shive culture solution and still others receiving Shive's solution modified with respect to nitrate. The total concentration of the Shive solution used in the chief wheat experiment was below that of Shive's " best " solution and had an osmotic pressure of approximately 1.3 atmospheres. Except as otherwise expressly noted, the solutions were not changed from the time of starting the experiment until the end thereof. No less than six culture jars with each kind of treatment were employed, thus permitting some control of the plants' variability, since there were thus thirty plants in every kind of treatment, or, as above indicated, in every sub-series.

The object in all of these experiments was to determine if the higher green plants, or, at least, if some of them, possess the power of fixing nitrogen from the air when the plants receive no nitrogen, or small, moderate, and large quantities of nitrogen in the solutions in which they are grown. It was further our purpose to determine the extent of nitrogen fixation, if any

should occur, and to note the behavior of plants under these circumstances.

The solutions employed in the cultures were made up as follows: Stock solutions were first prepared separately for each salt, Solution No. 1 containing 110 grams KH_2PO_4 per litre; Solution No. 2, 166 grams $MgSO_4$ per litre; Solution No. 3, 54.5 grams $Ca(NO_3)_2$ per litre; and Solution No. 4 being a saturated solution of $CaSO_4$. Baker's analyzed chemicals without purification were employed. Solutions for each sub-series of cultures consisting of 12 litres in bulk were then made up from the stock solutions as indicated for illustration in Table I. In the cases in which one-quart culture jars were used 950 c.c. of solution were available to the plants, whereas in the two-quart jars 1950 c.c. of solution were supplied.

In all cases, the pH of the solution at the start was 5.0 and increased toward the neutral point within a week from the beginning of the experiment.

At the end of the growing period allowed in each experiment, the plants from each jar were harvested and transferred, roots and tops combined, to a Kjeldahl digestion flask, sulphuric acid added and the digestion carried out by the modified Gunning method. The titrations were made as is customary, except that very dilute N/50 standard acid and alkali were employed when very small amounts of N were involved. In some series, the plants were dried at 100° C. after harvesting, and the total dry matter determined before the digestions were made and the nitrogen determined. These differences in procedure are indicated as used in the tables given below.

TABLE I.

Composition of Culture Solutions.

Sub-series No.	Proportion NO_3 Supplied.	KH_2PO_4 c.c.	$MgSO_4$ c.c.	$Ca(NO_3)_2$ c.c.	Mg. N per jar.	$CaSO_4$ c.c.
1	Full	200	200	200	200	...
2	3/4	200	200	150	150	835
3	1/2	200	200	100	100	1670
4	1/4	200	200	50	50	2505
5	1/8	200	200	25	25	2922
6	1/20	200	200	10	10	3173
7	1/50	200	200	4	4	3283
8	1/100	200	200	2	2	3307
9	None	200	200	..	..	3340

DESCRIPTION OF THE INDIVIDUAL EXPERIMENTS.

The experimental results obtained can be considered best in series, and we shall, therefore, proceed on that basis.

WHEAT SERIES A.

The jars in this series were prepared as indicated in Table I, except that the sub-series 8 consisted of twelve jars instead of six, with five plants each, as was true in every other sub-series. For that reason, the plants in six of those twelve jars were allowed to grow for ten weeks, whereas all the other plants in Wheat Series A were harvested after seven weeks. For the first week to ten days, the plants receiving no nitrogen in the culture solution behaved similarly to the others, as is well known to those who have grown plants under such conditions. After that period, however, the effect of nitrogen starvation became clearly apparent and increased for two weeks thereafter. In the third week, growth seemed to be at a standstill. The leaves were light green and very narrow, and there was no tillering. After the third week, new leaves began to appear as the old ones dried up and after that there was never a period in the growth of the plants in that part of Wheat Series A in which the plants did not show fresh green leaves which were short and narrow. The plants in sub-series 8 were, however, short and stunted and the total amount of growth made was slight. It is to be strongly emphasized, nevertheless, that in striking contrast with the case of plants grown in the absence of any other essential element, the plants grown without nitrogen in the culture solution, while starved and stunted, look healthy and keep on growing until they produce heads and can be kept thus, as our experience shows for a period of four to five months in a growing condition without the supply of any nitrogen to the culture solution. The results of the analyses in Wheat Series A are given in Table II.

With very few exceptions in which clearly there were losses of nitrogen due to faulty manipulation, the data in Table II show gains of nitrogen in every culture of the long series of data presented. Moreover, it will be noted that there were gains of nitrogen in the cultures whether they received an initial addition of nitrate to the culture solution or not. In fact, there is a steady increase in nitrogen gains in every sub-series until we reach the cultures with the full complement of nitrate, when we find a

TABLE II.

Wheat Series A.

Sub-series No.	Jar No.	N found, Mg.	Gain or Loss in N, Mg.
	1	193.63	−9.37
	2	226.50	23.50
1	3	199.14	−3.86
200 mg. nitrate N added per jar.	4	220.04	17.04
	5	231.72	28.72
	6	206.66	3.66
	1	123.61	20.61
	2	123.39	23.39
2	3	111.34	8.34
100 mg. nitrate N added per jar.	4	120.12	17.12
	5	124.81	21.81
	6	121.54	18.54
	1	66.57	13.57
	2	67.21	14.21
3	3	62.34	9.34
50 mg. nitrate N added per jar.	4	64.44	11.44
	5	65.83	12.83
	6	65.52	12.52
	1	36.02	8.02
	2	35.26	7.26
4	3	34.36	6.36
25 mg. nitrate N added per jar.	4	32.08	4.08
	5	31.32	3.32
	6	32.08	4.08
	1	17.02	4.02
	2	14.97	1.97
5	3	16.11	3.11
10 mg. nitrate N added per jar.	4	17.33	4.33
	5	18.32	5.32
	6	16.42	3.42
	1	8.83	1.76
	2	9.27	2.20
6	3	9.27	2.20
4.07 mg. nitrate N added per jar.	4	9.65	2.58
	5	9.35	2.28
	6	9.20	2.13
	1	6.62	1.55
	2	6.32	1.25
7	3	6.47	1.40
2.07 mg. nitrate N added per jar.	4	6.32	1.25
	5	6.32	1.25
	6	3.58	−1.49
	1	4.03	1.03
	2	3.81	.81
8	3	4.57	1.57
No nitrate N added per jar.	4	4.26	1.26
	5	4.11	1.11
	6	1.90	−1.10

marked decrease in gain over the preceding cultures in which only half the nitrate content of the best solution was supplied. Table II, therefore, furnishes unequivocal evidence that the cultures have all succeeded in adding to the amount of nitrogen in their constituent plants over that due to the content of nitrogen in the seeds and the solution plus the amount furnished as nitrate where such additions were given. These gains in nitrogen cannot be doubted, and it is only the manner of fixation which may be questioned, a point which we shall discuss below in detail. This is all true, despite the fact that the nitrogen content of the residual culture solution is not taken into account. Analyses of those solutions were carried out, however, and show very considerable amounts, except in the series which were not furnished with any nitrogen or with only very small amounts of nitrogen (sub-series 8). This would seem to indicate that the actual gains of nitrogen are really very large, relatively speaking, if the nitrogen content of the whole system is taken into account. It is worthy of particular mention that the gains in nitrogen while greater in the absolute in cultures receiving some nitrate, are far greater from the relative standpoint in cultures receiving no nitrogen. The absolute gains are so large in some of the sub-series and the cultures are replicated in each sub-series to such an extent as to leave no room for doubt that the gains are distinctly outside the limits of error, provided the nitrogen content of the seeds and chemicals used is properly controlled and known. This brings us to a consideration of that topic.

The total nitrogen content of the chemicals, including a trace probably present in the water making up the solutions, was .4 milligram, as found by making several determinations. Some of that nitrogen could hardly have been in a form assimilable by plants, but even if it is all so reckoned and added to the amount present in the seeds used and the total subtracted from the amount of nitrogen found at the end of the growing period, there remain the strikingly clear and universal gains shown in Table II. Twenty analyses of lots of five seeds each showed a range in nitrogen content of 2.57 milligrams to 2.93 milligrams with an average of 2.59 milligrams. Thirteen further analyses of groups of five seedlings, each of the age of those set out in the cultures, showed a range of 2.54 milligrams to 3.13 milligrams of nitrogen with an average of 2.61 milligrams. The maximum figure, 3.13, was

found in only one case. There was, in fact, only one other lot of seedlings, out of the thirteen, which approached a nitrogen content just above 3 milligrams. For these reasons, we have felt that in adopting 3 milligrams for the amount to be deducted from the nitrogen values found in the cultures, we were making a liberal

TABLE III.

Residual Nitrogen in Culture Solutions—Wheat Series A.

Sub-series No.	Jar No.	N gained in culture solution at end of growing period, Mg.	Sub-series No.	Jar No.	N gained in culture solution at end of growing period, Mg.
	1	2.32		1	.27
1	2	2.63	*5*	2	.84
200 mg. nitrate	3	3.84	10 mg. nitrate	3	Lost
N added per	4	3.46	N added per	4	.56
jar.	5	15.20	jar.	5	.84
	6	12.65		6	1.71
	1	1.71		1	.19
2	2	5.97	*6*	2	.11
100 mg. nitrate	3	2.32	4.07 mg. nitrate	3	.19
N added per	4	2.78	N added per	4	.09
jar.	5	2.55	jar.	5	.19
	6	1.64		6	.27
	1	1.33		1	−.04
3	2	1.64	*7*	2	−.19
50 mg. nitrate	3	5.52*	2.07 mg. nitrate	3	−.04
N added per	4	.80	N added per	4	−.27
jar.	5	.88	jar.	5	.11
	6	1.48		6	.04
	1	.65		1	.27
4	2	.46	*8*	2	−.04
25 mg. nitrate	3	3.16	No nitrate N	3	.11
N added per	4	1.11	added per jar.	4	−.27
jar.	5	.56		5	−.04
	6	1.03		6	Lost

*Roots affected by decay.

allowance for everything. This was particularly true since we have not included the nitrogen values of the residual solutions in our computations.

The reason for our not, in fact, including the nitrogen content of the residual solutions in our calculations is that in some of them, and especially in those receiving considerable quantities of

nitrate initially, the figures showed such irregularity as to make us hesitate to introduce them as a complicating factor into a situation which is perfectly clear without them. We do not wish to imply, however, that the factor in question as regards regularity is really a serious matter, since the irregularities are not appreciable or significant in the sub-series of greatest interest and value with respect to the question at issue. In support of this assertion, we give herewith in Table III the analyses for nitrogen on the residual solutions of Wheat Series A. The irregularities and "lost" determinations were due to difficulty in obtaining a sharp end-point in titration, a situation which is difficult to explain.

SUPPLEMENT TO WHEAT SERIES A.

As indicated in Table II, Wheat Series A was harvested after seven weeks of growth in the culture jars. In sub-series 8, however, there were twelve, instead of the usual six, jars receiving no nitrogen as was noted above. Therefore six of these jars were allowed to remain in the greenhouse until the plants were ten weeks old, after which the analyses were made. Table IV gives the results of this supplementary series grown without any additions of nitrogen, save those in the seeds and the traces in the chemicals used in making the culture solutions.

TABLE IV.

Supplement to Wheat Series A.

(Plants grown to maturity in absence of N.)

Jar No.	Dry Weight, Mg.	N Gained, Mg.	Per cent. N of Dry Weight.	Remarks.
1	170	1.21	.7	1 head
2	240	2.04	.85	1 head
3	300	2.04	.7	1 head
4	180	1.46	.81	2 heads
5	330	Lost	..	.....
6	280	2.26	.8	1 head

It is clear from Table IV that the data for sub-series 8 in Table II are not only confirmed but much strengthened. The additional three weeks' period of growth nearly doubled the gains of nitrogen shown in the "no-nitrogen" sub-series, so that approximately 38.04 per cent. of the nitrogen contained in the plants was obtained from the atmosphere, the absolute gain per culture being, on the average, 1.59 milligrams.

TABLE V.

Wheat Series B.

(Harvested after thirteen weeks' growing period.)

Sub-series No.	Jar No.	N Found, Mg.	N Gained, per cent.	Ave. N Found as per cent. of Dry Weight.
	1	402.24	...	
	2	318.7	...	
	3	346.03	...	
1	4	276.04	...	
404 mg. nitrate N	5	251.09	...	2.75
added per jar.	6	320.28	...	
	7	325.01	...	
	8	345.52	...	
	9	396.97	...	
	10	348.12	...	
	1	288.69	...	
	2	284.95	...	
	3	315.77	3.3	
2	4	228.80	...	
303 mg. nitrate N	5	286.17	...	
added per jar.	6	316.86	3.7	2.52
	7	277.13	...	
	8	243.07	...	
	9	334.64	9.5	
	10	270.69	...	
	1	Discarded	...	
	2	220.63	7.8	
	3	209.25	2.27	
3	4	197.96	...	
202 mg. nitrate N	5	207.94	1.55	1.92
added per jar.	6	203.58	...	
	7	Discarded	...	
	8	207.74	1.5	
	9	204.46	...	
	10	206.62	1.0	
	1	105.75	2.07	
	2	106.73	3.0	
	3	108.37	4.6	
4	4	112.21	8.3	
101 mg. nitrate N	5	112.88	9.0	1.16
added per jar.	6	Lost	...	
	7	108.88	5.1	
	8	109.48	5.65	
	9	109.82	6.0	
	10	107.29	3.55	

WHEAT SERIES B.

In order to determine how much larger additions of nitrate to the culture solution than those used in Wheat Series A affect the nitrogen-fixing power of the plant, if at all, and also to obtain further data on the validity of the results, a new series of cultures was prepared as follows: Five sub-series of jars were arranged with ten jars (four more replications than in preceding series) in

TABLE VI.

Wheat Series B.

Sub-series No.	Jar No.	Dry Weight, Mg.	Total N Found, Mg.	Per cent. N of Dry Weight.	Gain in N Mg.	Gain in N Per cent.	Remarks.
5 30 mg. nitrate N added. Harvested after 20 weeks.	1	6050	39.4	.65	6.8	17.3	
	2	6400	40.1	.63	7.5	18.7	
	3	6600	38.7	.60	6.1	15.8	
	4	6500	38.7	.60	6.1	15.8	
	5	6800	38.9	.57	6.3	16.2	
	6	6250	41.2	.66	8.6	20.9	
	7	5650	Lost	..	..	...	
	8	6100	39.4	.64	6.9	17.2	
	9	6650	38.0	.57	5.4	14.2	
6 No nitrate N added. Harvested after 24 weeks.	1	635	4.7	.74	2.1	44.7	3 heads
	2	460	4.5	.98	1.9	42.2	3 heads
	3	570	4.5	.80	1.9	42.2	4 heads
	4	455	3.9	.86	1.3	33.3	1 head
	5	580	4.6	.80	2.0	43.5	4 heads
	6	470	4.0	.85	1.4	35.0	3 heads
	7	575	4.4	.77	1.8	40.9	4 heads
	8	390	4.2	1.08	1.6	38.1	2 heads
	9	..	4.9*	..	2.3	...	
	10	..	4.69*	..	2.09	...	

*Grown for ten days longer than balance of series.

each sub-series. Each jar in sub-series 1 received 404 mg. N as nitrate; in sub-series 2, 303 mg. N as nitrate; in sub-series 3, 202 mg. N as nitrate; in sub-series 4, 101 mg. N as nitrate; in sub-series 5, 30 mg. N as nitrate; and in sub-series 6, no N as nitrate. This series was begun on November 11, 1922. The culture solution was changed on December 30, 1922. Our original intention in this series was to grow the plants to maturity, but we were obliged to harvest sub-series 1 to 4, inclusive, on February 10, 1923, because bacterial and fungus infections were destroying the roots and decomposing the organic matter with the production of the

usual poisonous substances of protein decomposition. Sub-series 5 and 6 were not so affected, however, and were harvested, respectively, after twenty and twenty-four weeks of growth. Owing to the long and vigorous growth of the plants in sub-series 5, a second change of culture solution was made February 15, 1923. Because of the somewhat different conditions obtaining in Wheat Series B for different sub-series, they were not all treated alike at harvest and therefore two tables are given. The first (Table V) deals with sub-series 1, 2, 3, and 4, and gives only the nitrogen found and nitrogen gained, if any, by each culture. The second (Table VI) deals with sub-series 5 and 6, and gives more detailed data with respect to the cultures.

Because of the encouragement given to putrefactive bacteria in the luxuriant root growth produced by large additions of nitrate to the culture solution, there were losses of nitrogen induced in the cultures which mar the data in Table V, and render them of little value. It is clear, nevertheless, in that table, that in spite of the serious difficulty in question, some of the cultures show small, but definite increases in nitrogen, even when as much as 303 milligrams of N as nitrate were furnished per jar to the culture solution. When, as in sub-series 4, only 101 milligrams of nitrate N were furnished per jar, there is a distinct gain in nitrogen in every culture. In sub-series 1, there were only losses of nitrogen, thus supporting the explanation given above.

Going on to a consideration of Table VI, we find an elaborate and striking series of data in support of the conclusions reached above as a result of the data in Wheat Series A. Whereas there was distinct and unequivocal evidence in sub-series 4 of Table V, to support the assertion that the wheat plant obtains and uses in its structure the free nitrogen of the air, the data in Table VI show very large relative increases in all cultures, including one hundred plants, in the nitrogen content of the plant over and above the amount furnished in the seed and in the solution. These are most emphatic and unexceptionable. Again, as in Wheat Series A, the percentage of nitrogen fixed as based on the total amount found, is the greater the less nitrate N is furnished to the culture solution initially. Again, therefore, we have evidence that the wheat plant grown in culture solutions containing small amounts of nitrogen as nitrate or no nitrogen at all, enrich themselves in nitrogen from an additional source than the seed and the

solution, which must, of course, be the immense store of N in the atmosphere. Several very significant facts stand out in such data in general, and in particular in those of Table VI. In the first place, the data of sub-series 6 are typical of a large group of data presented above, and of some to be presented below in that they testify to the large absolute amounts of nitrogen gained by the plant, presumably at the expense of the atmosphere. If this occurs in nitrogen-poor soils, as we have every reason to believe that it does, such fixation of nitrogen by wheat may be of much greater economic significance than casual inspection of such data as those in Table VI would lead one to believe. We shall take occasion to discuss this point more fully below. In the second place, the data in Table VI bring out the interesting fact that there is almost perfect accord between the amounts of dry matter produced in sub-series 5 and 6 per unit of nitrogen furnished. For example, there is a little more than twelve times as much dry matter produced in sub-series 6 as in sub-series 5, and about twelve times as much nitrogen is furnished in the first as in the second case. The form of nitrogen seems to have been of no significance in that regard, as must become obvious from a consideration of the forms of nitrogen available in each series.

In the third place, the greatest increases of nitrogen do not necessarily occur where the greatest amounts of dry matter are produced. We do not wish to emphasize this point to any extent, however, since certain chances for error are involved which have not been fully controlled in that particular respect in our experiments. This may have some relationship, however, to the mechanism of the nitrogen-fixation under discussion.

Finally, we come to a consideration of a very important point arising from our investigations in connection with Wheat Series B. While this has no direct bearing on the subject of this paper, it may be possessed of great significance in connection with several problems relating to the nitrogen nutrition of green plants. We refer to the differences found in the nitrogen content of the dry matter of the plants in the several sub-series in Tables V and VI. The average nitrogen content of these plants, along with the maximum and minimum found in each sub-series, are given in Table VI*B* for special consideration of that point.

The differences apparent in Table VI*B* as between sub-series 1, 2, and 3 are, in our opinion, real, but their significance cannot be

stressed in the face of the individual variations maintaining especially in sub-series 1 and 2. Despite all that, the general tendency in change in quality as regards nitrogen content of dry matter is perfectly clear. But, however that may be, there can be no question of the very marked depression in the nitrogen content of the dry matter as we proceed from sub-series 3 to sub-series 6. The fact that sub-series 5 and 6 had much longer growing periods than the other four, renders it futile to discuss the interesting question of ratio of nitrogen supplied to nitrogen found as between the different sub-series. For the same reason, the differences between sub-series 5 and 6 are not significant in one respect, because the second had four weeks more to grow than the first. Moreover,

TABLE VI*B*.

Percentage of Nitrogen in Dry Matter. Wheat Series B.

Sub-series.	Minimum.	Maximum.	Average.
1	2.23	3.13	2.75
2	2.20	2.87	2.52
3	1.50	2.40	1.92
4	1.00	1.32	1.16
5	.57	.66	.62
6	.74	1.08	.91

figures given above, and more to be furnished below, indicate clearly that under like conditions, the average nitrogen content of dry matter given for sub-series 5 is almost the same as that found in plants grown without any addition of nitrate nitrogen to the culture solutions. This, therefore, is the interesting point in the comparison of sub-series 5 and 6. *After a certain minimum supply of nitrate nitrogen is reached, further decrements from that amount to the point even of furnishing no nitrogen to the culture solution, are without effect on the nitrogen content of the dry matter.* Additions of nitrate nitrogen to the culture solution above that minimum are productive of marked increases in the nitrogen content of the dry matter produced.

WHEAT SERIES C.

From the behavior of the cultures in the foregonig series, we became interested to determine whether or not a *luxus* supply of nitrate in the culture solution could affect the nitrogen-fixing

power of the plants. We, therefore, arranged an elaborate series of cultures which were supplied with an excess of nitrate over that required by vigorous plants grown to maturity. In some of the jars, single plants, and in others three plants, were grown. It was our intention to grow these plants to maturity, but the vigorous root development in the presence of the excess of nitrate encouraged the growth of bacteria which decompose proteins, and after five or six weeks, the blackened and ill-smelling roots showed clearly that the cultures were of no value and had to be discarded. It will be remembered that in Wheat Series B, described above, we had the same experience with the cultures containing more than 101 milligrams of nitrate nitrogen, if attempts were made to grow the plants to maturity. It now seems clear that this type of experiment is feasible only under strictly aseptic conditions. Since it had no necessary relation to the main object of our experiments, we decided to postpone its repetition under the proper conditions, to some future date. It is impossible now to predict the results of such an experiment when properly carried out. Our experience would, however, incline us to the belief that there, too, nitrogen-fixation could be demonstrated as we have done above, under conditions of limited nitrate supply to the cultures.

WHEAT SERIES D.

It has been noted above that in Wheat Series A and B, the cultures were grown in the greenhouse atmosphere. In order to meet the criticism of the possible absorption by the plants of ammonia and nitrous acid from the air of the greenhouse, we decided to conduct an additional experiment with wheat plants in an atmosphere freed from ammonia and nitrous and nitric acids. Accordingly, we prepared eight jars with a somewhat reduced Shive solution (circa 1.3 atmospheres) but containing no nitrate. The wheat seeds were germinated and planted in the usual manner and then the culture jars were placed under a large bell-jar which was thoroughly sealed off from the atmosphere. By means of a suction pump, air, which was first drawn through a tower containing pumice covered with H_2SO_4 and then two towers containing $NaHCO_3$, was constantly renewed and supplied to the plants. This procedure permitted the plants to obtain all the CO_2 needed for photosynthesis and yet purified the air from all the ammonia,

nitrous acid and nitric acid which might be there. Recently we have made tests of the amount of ammonia present in the air employed and found it to be far too small to be of significance in our experiments in any case. The results obtained with Wheat Series D are set forth in Table VII.

TABLE VII.

Wheat Series D.

(Plants grown under bell-jar in purified air from January 1, 1923, to March 10, 1923.)

No Nitrogen Added to Culture Solution.

Jar No.	Dry Weight, Mg.	Mg. N Found.	Per cent. N of Dry Weight.	Gain in N Mg.	Gain in N Per cent.
1	510	3.78	.70	.82	28
2	535	3.93	.75	.97	33
3	515	3.77	.74	.81	27
4	570	4.19	.74	1.23	41
5	550	4.08	.74	1.12	37
6	505	3.53	.70	.57	20
7	545	3.96	.73	1.00	34
8	625	4.41	.70	1.45	50

The data in the foregoing table show with perfect clarity that the amounts of nitrogen fixed by the wheat plants in the foregoing series are not referable to ammonia, nitrous acid, or nitric acid nitrogen in the air. That oxides of nitrogen may have been obtained, nevertheless, is a possibility, but in the highest degree an improbability. The data also confirm those of the foregoing tables in that every culture shows a gain of nitrogen without exception, and in that the amount of nitrogen fixed is so large a percentage of the total nitrogen originally present in the seedlings plus the solution. This is the more striking since the amount of nitrogen in the culture solution at the end of the experiment, which averaged .3 milligram per jar, was not included in our computation. If this is added to the figures for increase of nitrogen, as it should be, the amounts of nitrogen fixed are significantly increased.

In this series, the roots and tops of the plants which were grown for ten weeks were perfectly healthy looking. The culture solutions were clear and there was no evidence of bacterial growth in the solutions or on the roots. Can there be any doubt from

these figures, and the statements made above, that wheat plants possess the power of fixing elementary, atmospheric nitrogen?

It should be remarked as an interesting fact incidental to Wheat Series D and to similar series of cultures, that the water requirement of plants grown in solutions without nitrate is very low, and that the percentage of dry matter in the matured plants is likewise strikingly high, just as the nitrogen content of the dry matter is strikingly low.

BARLEY SERIES.

The results obtained in Wheat Series A were so clear-cut and definite with regard to the power of the wheat plant to fix nitrogen that we deemed it advisable to test out other plants to see how general such a nitrogen-fixing power on the part of plants may be. We, therefore, arranged a series of barley cultures in all respects like those in Wheat Series A except that barley instead of wheat seedlings was used. The cultures were grown for seven weeks, and the conditions in the greenhouse, apart from temperatures, light, and humidity, were the same as those in the wheat series. The results obtained are given in Tables VIII*A* and VIII*B*.

There is no difference in essentials between the behavior of wheat and barley, as regards nitrogen-fixation as a comparison of Table VIII with Table II will clearly indicate. As regards unessential points, there are differences. For example, while the data in Table VIII show perfectly clearly the power of the barley plant to fix elementary nitrogen, they also show that it does not have the power to fix as much nitrogen as the wheat plant can fix in the presence of nitrates in solution. Otherwise, the two series are very similar and confirm each other on the nitrogen-fixing power of such higher green plants. Further discussion of the barley series would seem to be superfluous.

EXPERIMENTS WITH OTHER PLANTS THAN WHEAT AND BARLEY.

Among the other experiments on the possible nitrogen-fixing powers of the higher green plants, a number of series were carried out with *Pisum sativum, Bromus villosus,* and *Pinus* (species from southern New Jersey). We may now consider each of these separately, even though they were not studied completely and thoroughly as were the wheat and the barley. In the pea series, tap water was employed as the culture medium. The tap water contained combined nitrogen totalling 1 milligram per jar of

TABLE VIII*A*.

Barley Series.

Seven Weeks' Growing Period.

Average N in Original Seeds, 2.75 Mg. in Five Seeds.

Sub-series No.	Jar No.	N Found, Mg.	Average N Found, Mg.	Gain in Nitrogen. Mg.	Gain in Nitrogen. Per cent.
	1	200.99		Nos. 1 and 4 of this series are below total N originally in system. No. 4 had poor plants in comparison with others. Nos. 5 and 6 used for NO_3 determinations in plant sap.	
	2	215.22			
1	3	217.30			
200 mg. nitrate N added per jar.	4	180.15			
	5	.....			
	6	.....			
	1	105.06			
	2	108.10			
2	3	*99.55	106.15	3.4	3.2
100 mg. nitrate N added per jar.	4	106.76			
	5	107.46			
	6	103.57			
	1	55.15			
	2	58.78			
3	3	58.58	52.75	4.19	7.4
50 mg. nitrate N added per jar.	4	56.68			
	5	53.67			
	6	58.67			
	1	30.78			
	2	31.45			
4	3	37.64	32.36	4.61	14.2
25 mg. nitrate N added per jar.	4	31.95			
	5	32.09			
	6	30.23			
	1	13.81			
	2	13.88			
5	3	14.37	13.77	1.02	7.4
10 mg. nitrate N added per jar.	4	13.96			
	5	13.52			
	6	13.08			
	1	7.69			
	2	7.25			
6	3	7.55	7.46	.61	8.1
4 mg. nitrate N added per jar.	4	7.98			
	5	7.33			
	6	6.94			

*Not included in average.

TABLE VIII*A* (*Continued*).

Barley Series.

Seven Weeks' Growing Period.

Average N in Original Seeds, 2.75 Mg. in Five Seeds.

Sub-series No.	Jar No.	N Found, Mg.	Average N Found, Mg.	Gain in Nitrogen. Mg.	Gain in Nitrogen. Per cent
7 2 mg. nitrate N added per jar.	1	5.50	5.57	.81	14.6
	2	6.05			
	3	5.50			
	4	5.55			
	5	5.70			
	6	5.14			
8 No nitrate N added per jar.	1	3.76	3.61	.85	24.0
	2	3.61			
	3	3.10			
	4	4.05			
	5	4.26			
	6	2.89			

TABLE VIII*B*.

Illustrative Data on Weights and Nitrogen Content in Barley Series.

Sub-series No.	Jar No.	Green Weight Tops, Gm.	Dry Weight Tops, Gm.	Per cent. Green Weight.	N as per cent. Dry Weight.
1 200 mg. nitrate N added per jar.	1	8.0	1.54	19.3	2.4
	2	11.9	1.72	14.5	1.9
	3	7.35	1.34	18.2	2.1
	4	8.8	1.42	16.1	2.3
	5	8.8	1.57	18.0	2.1
	Roots	..	2.84	...	1.9
2 100 mg. nitrate N added per jar.	1	4.25	1.07	25.2	1.5
	2	3.8	.96	25.3	1.4
	3	3.1	.80	25.8	1.6
	4	3.55	.88	24.8	1.55
	5	4.2	1.05	25.0	1.6
	Roots	..	2.35	...	1.5
3 50 mg. nitrate N added.	1	2.5	.65	26.0	1.3
	2	2.4	.59	24.6	1.5
	3	2.7	.73	27.0	1.7
	4	2.3	.61	26.5	1.3
	5	1.5	.38	25.3	1.6
	Roots	..	1.36	..	2.4

950-c.c. capacity. Three seedlings were set out in every jar. The nitrogen content of the pea seeds used was extremely variable and the average of 20 determinations on three peas each gave a value of 22.6 milligrams. The plants were grown to maturity, and all of them produced pods with normal seeds. At maturity, the roots and tops of the pea plants from every culture jar, of which there were twenty, were placed in Kjeldahl digestion flasks

TABLE IX.

Pisum Sativum Series.

(Harvested after eight weeks' growth.)

Jar No.	Dry Weight, Mg.	Mg. N* Found.	Per cent. N of Dry Weight.	Gain or Loss of N, Mg.
1	1.05	20.34	1.94	−3.26
2	1.20	24.80	2.07	1.20
3	1.15	21.27	1.85	−2.33
4	1.10	20.42	1.86	−3.18
5	1.10	23.05	2.09	− .55
6	.85	19.88	2.34	−3.72
7	.85	18.86	2.22	−4.74
8	1.30	25.50	1.96	1.90
9	1.00	19.48	1.95	−4.12
10	1.35	26.98	2.00	3.38
11	.80	18.39	2.30	−5.21
12	1.05	21.51	2.05	−2.09
13	.95	20.14	2.12	−3.46
14	1.20	22.32	1.86	−1.28
15	1.45	24.92	1.72	1.32
16	1.10	Lost	...	...
17	1.20	22.91	1.91	− .69
18	...	21.75	...	−1.35
19	...	18.20	...	−5.40
20	...	24.50	...	.90

*Original N = 22.6 mg. for three peas, plus 1.0 mg. for N in a jar of tap water, making a total of 23.6 mg.

and digested, after which the usual nitrogen determination was made as in the case of the wheat and barley. Table IX sets forth the results obtained.

It is perfectly clear from Table IX that there is no evidence that the pea plant, under the conditions named, possesses the power of fixing atmospheric nitrogen. While there are a few figures which indicate gains in nitrogen, they cannot be accepted as such, owing to the marked variability of the nitrogen content of the

pea seeds used. It should be clearly understood, however, that the figures in Table IX do not prove that the pea plant may not possess the power of fixing elementary nitrogen. The figures merely indicate that in the case of the pea plant, further studies need to be made, and statistical methods employed which will give definitely the limits of values for nitrogen outside of which gains may be taken as bona fide ones. The experiment with peas is, therefore, to be regarded as inconclusive. The results are, however, interesting in support of the wheat and barley figures from the aspect of the possible intervention of bacteria in the nitrogen-fixation process. This will be discussed below.

TABLE X.

Bromus Villosus Series.

(Harvested after eleven weeks' growth.)

Jar No.	Dry Weight, Mg.	Mg. N Found.	Per cent. N of Dry Weight.	Gain in N Mg.	Gain in N Per cent.
1	250	1.7	.68	.1	6.8
2	350	1.9	.54	.3	15.8
3	350	2.0	.57	.4	20.0
4	350	2.0	.57	.4	20.0
5	300	1.7	.57	.1	6.0
6	350	1.8	.51	.2	11.1
7	300	1.8	.60	.2	11.1
8	350	1.7	.48	.1	6.0
9	250	*1.4	.56	..	..
10	300	Lost	..	..	..
Ave.	322	1.8	.56	.23	12.8

*Not included in average.

In the case of the *Bromus,* the results were much less variable than those of the peas. In this case, the experiment was carried on as in Wheat Series B. A Shive solution with a limited nitrogen supply as shown in Table X and of reduced total concentration (circa 1.3 atmospheres) was employed in the culture jars. Five seedlings were set out in every jar and ten jars were used in the experiment. The nitrogen content of five seeds as determined by several determinations was 1.6 milligrams. The plants were grown eleven weeks. The results obtained are given in Table X.

It is apparent from Table X that if *Bromus* possesses the power of fixing elementary nitrogen, it is a very small power under the conditions of the experiment. It is, of course, impossible to

assert that the nitrogen-fixing power of *Bromus* might not be much enhanced by the addition of more nitrate nitrogen to the culture solution. Moreover, even in our experiment, the nitrogen content of the culture solution was not taken into account or the amounts fixed would have been larger. Even with all these reservations, it may be said that the figures in Table X, while to some extent variable, and in the absolute very small, indicate a nitrogen-fixing power on the part of *Bromus villosus*. It is to be noted that in every culture with five plants, there was a gain of nitrogen, even though it was small. This, therefore, is consonant with the figures for wheat and barley, though being much less conclusive than the latter.

Finally, we may say a word about a very incomplete experiment with *Pinus*. Some seeds were obtained from southern New Jersey. The seeds were germinated and set out in two-litre jars, three seedlings per jar. The solution used was tap water of the same type as that described above for the pea experiment. Six such jars were prepared. The seedlings were planted on April 25, 1923. They are still growing in the original solution in July, 1924. New leaves are being produced constantly. The total nitrogen at the disposal of these plants consisted of 1.62 milligrams in the three seedlings set out per jar, and 1.8 milligrams in the tap water. Since no analyses of these cultures have been made, it would be useless to discuss them at length. It is remarkable, however, that they have produced steady, though very slow growth, until they have reached a height of two and a half inches on the small quantity of nitrogen which is mentioned above. The roots have developed to the usual great length which characterizes plants growing in solutions devoid of nitrogen. We are not unmindful that in the case of *Pinus*, mycchoriza may play a part in the nitrogen-fixation process and therefore do not desire to draw any conclusions from this experiment. We hope to make a much more thorough study of *Pinus* later and shall then be prepared to make more definite statements with respect to it. Meanwhile, we present the meagre results thus far obtained as very interesting evidence of the ability of pine seedlings to grow for more than a year in an unchanged tap water solution with only about 3.4 milligrams of nitrogen at the disposal of three plants per jar.

AN ANALYSIS OF CRITICISMS OF SUCH EXPERIMENTS.

In all the discussions and interpretations of experimental evidence bearing on the question of whether or not green plants without the aid of bacteria possess the power of fixing atmospheric nitrogen, there are clearly two diametrically opposed views. This situation renders it obvious that somewhere underneath the surface of all that has been said and done on this subject, there lurk circumstances which, if brought to light, would cut the Gordian knot and render a verdict in favor of one or the other view. It seems clear to us that allowing for the idiosyncrasies and individual characteristics of species, only one of the views in question can, in general, be correct. The dissidence which marks the views concerned in the controversy is clearly referable to some error in experimental procedure or interpretation. In addition to the experimental evidence which we ourselves have contributed toward the solution of this vexed problem, and which we have discussed above, we have set for ourselves the task of appraising the investigations of others in the same field through a critical study of their results, and of giving an answer to those criticisms which have been directed against the investigations which are presumed to furnish proof of the existence within the green plant of the power to fix elementary nitrogen from the atmosphere.

In the case of the older investigations, we may first examine the evidence of the kind furnished by Boussingault, and by Lawes, Gilbert, and Pugh. The nature of the Boussingault experiments was such that accuracy of nitrogen determinations in the sense in which we would accept that term was clearly insufficient to allow of accurate judgments. Pot experiments and field experiments had not reached in Boussingault's day, and perhaps have not even arrived to-day at that state of perfect control which would invest results obtained with them with any particular significance when small differences in nitrogen content are of absolute importance. Even the results of Lawes, Gilbert, and Pugh, which are based on very much more careful analytical evidence than any of those obtained by Boussingault, are clearly inadequate and inconclusive. For example, the fact that Lawes, Gilbert, and Pugh employed the old soda-lime method for the determination of total nitrogen, would, in itself, seem to render highly questionable the value of the differences which they discuss between the nitrogen content of the cultures at the start and the nitrogen content of the cultures

at the end of the growing period. Anyone who has had experience with nitrogen determinations by the combustion method cannot help but be impressed with their utter uselessness for judgments depending on small differences in nitrogen content. Besides, Lawes, Gilbert, and Pugh used, in some of their experiments, soil made by the burning of clay. The difficulty of the complete eradication of the organic nitrogen by burning the soil can only be understood by those who have tried to remove all traces of nitrogen from soil through ignition. If this difficulty is added to the variability in soil samples as regards nitrogen, even when it is possible to obtain all the nitrogen by the analytical procedure involved, and to the weakness of the combustion method for determining nitrogen besides, the results of Lawes, Gilbert, and Pugh lose whatever little significance they may have at any time possessed. Reference to the work of Waynick,[8] and of Waynick and Sharp [9] will strengthen the foregoing statement and convince those who have any doubts on the subject. Very much the same kind of criticism may be directed against the ground-up earthenware pots which were used in other experiments of Lawes, Gilbert, and Pugh.

In addition to all this, very little attention has been paid by writers on the subject, in the past, to the great variability which characterized the results obtained by Lawes, Gilbert, and Pugh. Our study of their original papers makes it perfectly clear to us that a great many results were obtained which showed slight nitrogen-fixation, even though many others were obtained which showed no nitrogen-fixation. With such a state of affairs confronting us, and with the criticisms of methods employed, which, owing to brevity of space, have only been considered very cursorily, it seems surprising that Lawes, Gilbert, and Pugh should have made the following statement: "In fact, so far as our labors with these plants bear upon their experiments (Boussingault and Ville) they could not have given a more decided result." Another point of weakness in the Lawes, Gilbert, and Pugh experiments consisted in their having employed an amount of ash to mix with their burnt clay, which yielded very strong salt solutions, and which varied approximately between 10 and 20 per cent. solutions of ash. No one acquainted with the effects of great concentrations of salts on plants in these days would ever attempt to use such strong salt solutions in a crucial experiment on the important

point of whether or not elementary nitrogen may be fixed by green plants, or for that matter in any other experiment of a similar nature. Then, too, in the case of the control of the nitrogen content of the seeds employed in the experiments, their statements show that a very large number of seeds were used together as one sample for the determination of the average nitrogen content of the seed. In a few cases only, a few seeds were used upon which to make the determination of the average nitrogen content of the seeds employed in the experiment. Considering the Lawes, Gilbert, and Pugh, and Boussingault experiments as a whole, therefore, from the points of view discussed above, it seems impossible to accept their judgments in the question at issue as final. Nay, more, it is incomprehensible to us that in the light of our present knowledge, they can be accepted as of any value at all in respect to the actual settlement of the main question. It is also surprising to note that the examination of Ville's experiments by a special committee appointed by the French Academy with the result that a verdict was given in favor of his contentions, should have been so largely overlooked by writers on this subject and should not have been accorded at least the same recognition which has been given to Boussingault, and to Lawes, Gilbert, and Pugh. For purposes of a definite and accurate solution of the problem of whether or not green plants are possessed of the power of fixing elementary nitrogen from the atmosphere, the results obtained during the last century would seem to us to be entirely nugatory.

Beginning with the results of the present century, we may proceed to an appraisal of each set of experiments in this controversial field. The experiments of Jamieson, beginning with his reports of 1905, can, it appears to us, be said to be of no more value than those of the nineteenth century. In fact, in some respects, they are distinctly less accurate and therefore of little importance for a final judgment. Jamieson has, moreover, rendered his own claims the more questionable by the introduction of his theory on albumin generators which has been proved since to be wholly untenable. The experiments of Moore and Webster,[10] and those of Moore, Webster, and Whitley were unfortunately confined to the algæ. Since the algæ occur so universally with bacteria and since, what is more important, the total amount of dry matter and hence of total nitrogen involved is so small, even the more accurate nitrogen determinations which in these days can be made,

as compared to those of Lawes, Gilbert, and Pugh, would render it of the greatest difficulty, if not impossibility, to be able to speak with authority and finality on the question at issue with such experiments as a basis. As regards the experiments of Wann, in which the investigator claims to have proved only when nitrate was supplied, that *Chlorella* possessed the power of fixing nitrogen from the air, it may be said that the recent experiments of B. Muriel Bristol and H. J. Page [11] have definitely shown a source of error in Wann's experiments as regards the analytical procedure involved, which would seem to throw his results "out of court" so far as the decision on nitrogen-fixation by algæ is concerned.

We may now consider the work of Mameli and Pollacci. With a variety of plants belonging to a diversity of orders from the algæ to the phanerogams and with methods which seem to leave little to be desired, Mameli and Pollacci have proved, beyond a peradventure, that many, if not all, green plants, possess the power of fixing elementary nitrogen from the air. They worked with plant cultures which were treated so as to be free from bacteria, and they supplied air to the plants which was freed from ammonia and other nitrogen compounds. They measured the amount of elementary nitrogen at the beginning and at the end of the experiment and found that fixation of nitrogen corresponded to loss of elementary nitrogen from the space in which the plants were growing. They used a modern method for the determination of the nitrogen content of their cultures and of their materials. These experiments constitute the only ones on record which, considered from any point of view, may be regarded as having definitely established the fact that many green plants possess the power, unaided by bacteria, of fixing elementary nitrogen from the atmosphere. Whatever may be said, therefore, of the experiments of Jamieson, of Moore, Webster, and Whitley, and of others who have attempted to prove that plants do possess the power of fixing nitrogen, certainly that criticism cannot be directed against the experiments of Mameli and Pollacci. The fact that Molliard,[12] working under conditions free from bacteria, obtained no fixation of nitrogen by radish plants which he grew, does not in any way disprove the discovery resulting from the far more extensive experiments of Mameli and Pollacci. It was in support of these experiments, and because of their validity, that we carried out the experiments which are described above, and for which

we used plants of economic importance which Mameli and Pollacci had not employed. It was our object to see to what extent such plants possessed the power of fixing nitrogen and since Mameli and Pollacci had indicated by their results that bacteria were not necessary to the fixation of nitrogen by green plants, we paid little heed to that feature of the experiment. Before going on to a critical examination of the bacterial hypothesis involved in this controversy on nitrogen-fixation, we wish to say, therefore, that our experiments are in accord with those of Mameli and Pollacci to the effect that some green plants, at least, are possessed of the power of fixing nitrogen from the atmosphere.

A CRITIQUE OF THE OBJECTION THAT CULTURES MUST BE STERILE IN ANY EXPERIMENTS DESIGNED TO SHOW WHETHER OR NOT GREEN PLANTS POSSESS THE POWER OF FIXING NITROGEN.

It will be remembered that we have proved above that the cultures of wheat and barley in the absence of a *luxus* nitrate supply, without exception, showed gains in nitrogen. We stress the phrase " without exception," since it is striking that with all of the errors to which human experimentation is subject, we should have succeeded in such a large number of cultures in showing gains of nitrogen in every case. Moreover, we showed that in many of our cultures where the plants were supplied with some nitrate nitrogen, the amounts of nitrogen fixed were not only large from the relative standpoint as they were in the case of other cultures, but were very considerable from the absolute standpoint. Our method for determination of nitrogen by the modified Gunning procedure has been so far refined that it is not subject to errors of any great magnitude. (See Waynick and Sharp.) All this being true, there can be no question that we have proved, at least in the case of wheat and barley, that our cultures gained nitrogen and gained it at the expense of only one source, namely, the elementary nitrogen of the air. No one can question the correctness of this conclusion. There can be no ground upon which the challenge thereof can be made. Critics of our experiments and of similar experiments have, therefore, been forced to the one criticism which remains to them, namely, that we did not work with sterile culture solutions, or sterilized seedlings, and hence the gains of nitrogen in our cultures may be due

to fixation of nitrogen by bacteria which were invisible, but working on the root cells. One statement in this criticism is, of course, correct. We did not employ sterile solutions and we did not sterilize our seeds. The balance of the statement we can show to be without justification or validity by the following discussion of the experiment and logic.

(1) Salt solutions, such as we used in our experiments and which we described in detail above, are known to be wholly unfit for the life and activities of hetrotrophic bacteria which all forms of nitrogen-fixing bacteria must be.

(2) If it should be considered that the bacteria are living in such solutions, not on the constituents of the solution itself, but upon the root cells or their exudates, if any, then we must at least assume the presence of a sufficient amount of carbonaceous material to furnish the energy for the fixation of nitrogen in the quantities noted in the tables which we have furnished above. No nitrogen-fixing bacteria of any kind have yet been discovered which have manifested a greater efficiency at nitrogen-fixation than is represented by the ratio of one gram of sugar or of mannite for every fifteen milligrams of nitrogen fixed. Even this figure has been reported in only one case and is to be regarded definitely as of questionable application for ordinary conditions under which bacteria may grow and fix nitrogen. When it is observed in the tables which we have furnished, that there is so little total dry matter produced as compared with the amount of nitrogen shown to be gained by the cultures, it seems impossible to account for the source of the carbon on the basis of which the alleged nitrogen-fixing bacteria in the cultures could have fixed the nitrogen which has been shown to be fixed. In the cultures receiving no nitrate nitrogen, there was sufficient nitrogen fixed to require the use of as much carbon as was contained in the roots and tops of the whole plants, and more besides. This makes it obviously absurd to assume that the nitrogen gained by the plant is referable to fixation by bacteria.

(3) Microscopic examination of scrapings from the roots, and examination of the culture solution itself, showed a very sparse bacterial population. Obviously for any efficient nitrogen fixation, there would have to be a large bacterial population, to judge from what we know of bacterial fixation of nitrogen to-day.

Moreover, of the few forms and small numbers of bacteria which were found on the roots and in the culture solution, there is none that had the slightest resemblance to any of the known forms of nitrogen-fixing bacteria.

(4) In order to strengthen all this, however, we prepared media made from ground-up roots of the plants grown in some of our cultures. In such root extract agar, by plating out 1 c.c. of the culture solution in which the roots had been thoroughly washed, a few very tiny colonies of bacteria appeared. This, again, would seem to indicate that the media in question are unsuited for bacterial growth and to prove that there could not have been a sufficient number of bacteria in the plant cultures to have any significance.

(5) With dextrose and mannite solutions made up like the plant culture solutions in other respects, but furnished with an abundance of dextrose and mannite, the roots of the wheat plants or of certain fractions of the culture solutions, produced good bacterial development. This was sufficiently good to make the solution entirely turbid. In these cultures, grown for periods of three weeks, no organisms like the usual nitrogen-fixing bacteria were found. None of the reactions of such bacteria which are commonly known to bacteriologists were obtained in these solutions. Finally, analyses of these cultures showed a slight loss instead of a gain in nitrogen. This would indicate, once more, very clearly that no nitrogen-fixing bacteria were involved in the cultures or could have had anything to do with the gain of nitrogen which we have noted.

(6) If the nitrogen gained by our cultures was due to the fixation of nitrogen by bacteria, it seems hard to explain why the plants grown with an excess of nitrate furnished to the culture solution and in which the roots at a certain stage in the plant's life began to decay, there should not have been the greatest amount of nitrogen fixed, since the bacterial growth was so pronounced. These were the very cultures in which there were losses of nitrogen or, at any rate, no gain.

(7) What is even more important than the observation under No. 6 is the fact that there were no gains of nitrogen found in the cultures of *Pisum*. Since the roots of *Pisum* are naturally adapted to symbiosis with *Bacillus radicicola*, and since the chemical composition, particularly as regards nitrogen, of such pea

roots would seem to be particularly favorable for the growth of heterotrophic bacteria, one would expect that there, if anywhere, nitrogen-fixing bacteria would cause the cultures to increase in nitrogen content. These, however, are precisely the cultures in which there were no gains of nitrogen, and, in fact, many of them showed losses of nitrogen.

(8) If the nitrogen fixation noted in our cultures is due to bacteria which used root cell exudates as a source of carbon, the amount of nitrogen fixed should increase with the extent of the root system. We have every evidence, however, that with large increases in the surface of the root brought about by nitrate supplies, there seems to be a decrease in the efficiency of nitrogen-fixation.

(9) No one has thought of criticizing Lawes, Gilbert, and Pugh's experiments usually referred to as the "classical experiments on nitrogen-fixation" from the viewpoint of the possible existence of bacteria in their cultures. If their results are to be accepted as having authentically and finally proved that green plants cannot fix atmospheric nitrogen, are their results to be uncriticized from the bacteriological point of view?

(10) Finally, Mameli and Pollacci grew their plants under sterile conditions and yet proved nitrogen fixation with most of the plants which they studied. We do not wish to be understood, however, as believing that the cultures used by Mameli and Pollacci were absolutely free of bacteria. We have not seen an account of any experiments and cannot at the present time conceive of any in which the absolute and unquestioned eradication of bacteria from cultures for studying whether or not green plants have the power of fixing nitrogen can be accomplished. Anyone who has had sufficient experience with the technique of such experiments as those under consideration, will, on mature reflection, realize the pointed character of this last observation.

(11) In connection with all of these observations, it is to be noted, further, that the criticisms of Roach and Page with regard to Wann's experiments will not hold for our results, since we have demonstrated gains of nitrogen in cultures which had no nitrate whatever to start with and in other cultures in which the nitrate supply was so limited as to have been entirely transformed long before the analyses were made into the organic nitrogen of the plant tissue.

In general comment on the whole question involving possible experiments on the fixation of nitrogen in plant cultures by bacteria, we would like to observe that, in our opinion, the world of plant physiology has made a fetish of limiting nitrogen-fixation to bacteria. There is very little reason known to science why the bacterial cell should be the only living cell to possess the power of fixing nitrogen. It would seem to be the most natural thing in the world, as Mr. Jamieson and others have observed, that the cells of green plants should possess the power of fixing elementary nitrogen, and we insist again, that we, as well as Mameli and Pollacci, and perhaps others, have proved that some green plants, at least, do possess the power of fixing elementary nitrogen from the atmosphere. In spite of that, however, and of our conviction with regard to the matter, we are planning experiments at the present time under as nearly sterile conditions as can be had, with wheat and barley plants, which are aimed to give further support to our thesis.

THE SIGNIFICANCE TO THE PLANT WORLD OF NITROGEN-FIXATION BY GREEN PLANTS UNAIDED BY BACTERIA.

Assuming that we have proved the existence of the power in the green plant to fix elementary nitrogen from the atmosphere, the question arises whether or not such fixation of nitrogen is of a magnitude which is significant either from the point of view of maintenance of natural flora or from the economic or agricultural standpoint. Those who observe the dwarfed, obviously undernourished plants, with the characteristic long root produced by plants grown without nitrate in culture solution would, of course, say that whatever nitrogen may be fixed from the atmosphere by such plants cannot be considered as of vital importance to the maintenance of plants in nature when no nitrates are present. This would, at first blush, seem to be the truth, but on careful reflection becomes very questionable. In the first place, it must be remembered that whatever amount of nitrogen is fixed (in say a soil which is initially entirely free from nitrogen) by the first generation of plants is a clear and definite gain for the benefit of the second generation. With this as a basis, the second generation of plants may be enabled to fix more nitrogen than would the first generation. In this wise, conditions will be even better for the third generation of plants and so on up to a point where the soil, under the proper conditions, may become so well supplied

with nitrogen and organic matter as to suffer losses of nitrogen from other causes which supervene. When it is remembered, further, that in nature we do not start with a soil which is absolutely free from nitrogen, but with soil of one kind or another which contains some nitrogen, thus giving plants more like the stimulus which is found in some of our cultures described above as having some nitrate in the culture solution, the absolute fixation of nitrogen may be expected to be much larger from the start and thus be of great significance in the life of a given generation of plants and of succeeding generations thereto. It is not at all impossible, therefore, that much of the nitrogen supply of the earth was due originally to the fixation of nitrogen by green plants in some such way as is briefly imagined in the foregoing statements. The experiment still remains to be carried out, and we hope to accomplish it—in which the ideas which we just stated may be put to experimental test. There are many observations which we have not discussed, which lead us to believe that fixation of nitrogen at the earth's surface is constantly going on apace through the agency of the green plant. That bacteria, too, may contribute significantly to the nitrogen supply of the earth's surface, is, of course, quite possible, and even probable, but that is a point which does not require discussion here.

SUMMARY.

1. Experiments carried out with wheat and barley in culture solutions with, and without, nitrate nitrogen proved conclusively that the cultures gained nitrogen at the expense of the elementary nitrogen of the atmosphere.

2. Partial experiments with other plants resulted as follows: Peas have not shown the power to fix nitrogen under similar conditions, while *Bromus* shows a slight power to fix nitrogen.

3. A critical discussion of the results of other investigators, and a comparison of them with our results and those of Mameli and Pollacci are given.

4. Extensive arguments are given to prove that the nitrogen gained by our cultures at the expense of the nitrogen of the air was not first fixed by bacteria and then passed on to the plant. The fixation of nitrogen must have occurred directly, and probably occurs in the cells of the green leaves.

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Tupelo as a Pulp Wood. (U. S. Department of Agriculture, Press Service, September 20, 1924.)—A study of the growth of tupelo in second-growth stands has for some time been under way in the South, and the members of the Southern Forest Experiment Station who have it in hand hope soon to be in a position to make the results public. The importance of the study, according to the United States Forest Service, lies in the fact that a mixture of half tupelo and half southern pine has been found to produce an excellent quality of book paper. The consequent interest in this wood on the part of the pulp and paper industry warrants obtaining exact information regarding its growth and yield.

The South has furnished pulp wood in the past, but only for the manufacture of wrapping paper, containers, and similar products. If tupelo comes up to its promise as an important pulp wood, it is expected that the result will be of benefit both to the paper industry and to the timber owners of the South. R.

STUDIES IN PHOTOGRAPHIC SENSITIVITY.*

IV. EFFECT OF OXIDIZERS ON THE SENSITIVITY AND ON THE LATENT IMAGE.

BY

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THE principal facts [1] determined as to the action of chromic acid on the sensitivity and on the latent image, on both ordinary plates and on one-grain-layer plates, are:

(1) Chromic acid has a greater effect on the latent image than on sensitivity.

(2) Chromic acid does not completely destroy sensitivity.

(3) When treated with comparatively strong potassium iodide solution (0.5 per cent.) the sensitivity of the grains to ordinary developers is lowered considerably.

(4) When a plate which has been treated with chromic acid is then treated with iodide, no greater effect is produced than with iodide alone.

(5) But when a second chromic acid treatment is given following the CrO_3-KI treatment, sensitivity is practically completely destroyed, at least no trace of image, even when the grains are examined at ×10,000 magnification, is produced with 16,000 times the exposure necessary for the formation of the first perceptible image (visually) on the untreated plate.

Provisional conclusions drawn from this work are that:

(1) Internal and external "sensitive nuclei" exist in the grain prior to exposure. These may be identified with the "silver germs" postulated by Lüppo-Cramer [2] and others,[3] but may have a different nature.

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* Communicated by Dr. S. E. Sheppard, Acting Director. Presented in abstract before the American Chemical Society, Milwaukee meeting, September, 1923, and published as communication No. 210 from the Research Laboratory, Eastman Kodak Company.

[1] S. E. Sheppard, E. P. Wightman and A. P. H. Trivelli, JOUR. FRANK. INST., **196**, 779, 802 (1923).

[2] *Cf.* Lüppo-Cramer, "Kolloid Chem. u. Photographie," 2nd Ed., Dresden, 1921.

[3] S. E. Sheppard, *Phot. Corresp.*

(2) The surface nuclei only are removable by chromic acid either prior to or after exposure.

(3) The occluded nuclei can be uncovered by potassium iodide of sufficient strength which shaters the grain completely.[4]

(4) The nuclei so uncovered can then be destroyed by further treatment with chromic acid prior to exposure, thus practically destroying sensitivity.

While fairly strong solutions of iodides lower the sensitivity of plates to the same developer, very dilute solutions tend to supersensitize them and cause greater tendency to fog. This has been attributed by Sheppard and Meyer [5] and by Sheppard [6] to the greater specific adsorptive power of iodide for both nascent silver and for the developer, as well as to the orienting effect of the iodine ion in the silver halide crystal lattice rather than to mechanical rearrangement of colloid silver nuclei.

Now there are certain other fundamental facts concerning the photographic plate which have become well established, and with which the above conclusions seem to be in harmony.

(1) The existence of impurities, generally silver, in the silver halide grain has been repeatedly asserted by various investigators.[7]

(2) The first observable effect of light is the formation—in molten silver halide—of a cloud of ultra-microscopic particles,[8] both on the surface and inside the mass. These increase in size with increasing exposure until they are large enough to be visible in the ordinary microscope. Trivelli and Sheppard have observed microscopically a quite similar formation and growth of discrete spots in solid crystals of silver halide with increasing exposure to light.[9] The spots continue to grow to a comparatively large size as distinct entities, spots close together, however, finally

[4] *Cf.* F. F. Renwick, *J. Soc. Chem. Ind.*, **39**, 156T (1920).

[5] S. E. Sheppard and G. Meyer, *Phot. Jour.*, **60**, 12 (1920).

[6] S. E. Sheppard, *Ibid.*, **62**, 88 (1922).

[7] For references see "The Silver Bromide Grain of Photographic Emulsions," by A. P. H. Trivelli and S. E. Sheppard (Eastman Kodak Company and Van Nostrand, 1921).

[8] R. Lorenz, *Z. Elektrochem.*, **7**, 277 (1900); R. Lorenz and W. Eitel, *Z. anorg. Chem.*, **97**, 57 (1915); **92**, 27 (1915); *Koll. Zeit.*, **22**, 103 (1918).

[9] A. P. H. Trivelli and S. E. Sheppard, "The Silver Bromide Grain, Etc.," Monograph No. 1, Eastman Kodak Company, April, 1921, pp. 83–84; *Phot. Jour.*, **63**, 334 (1923).

coalescing. New smaller ones in the meantime appear and also continue to grow. The grain never becomes gradually blacker and blacker uniformly over its entire surface.

(3) That there is a definite decomposition of silver halide to silver and bromine with prolonged exposures has been abundantly proved by the work of Lüppo-Cramer,[10] Koch and Schrader,[11] Ehlers and Koch,[12] Schwarz and Stock[13] and a number of others.[14]

(4) In 1911, Chapman Jones[15] showed that with exposures which would not produce a visible image, it is possible, by very short time development, to partially reduce the silver halide and form silver particles in it too small to be visible microscopically, yet which impart color to the emulsion, and which particles could be developed further by means of mercury until visible in the microscope.

Before this, in 1907, Scheffer[16] had noticed that development starts and proceeds from discrete points on or in the grain. Hodgson,[17] Svedberg,[18] Toy[19] and others have since studied this fact much more in detail. Among other things, Svedberg found that the development spots are distributed at random among the grains according to the laws of chance.

(5) It has been known for a long time that certain chemical reagents, such as hydrogen peroxide, sodium hypophosphite, sodium arsenite, and a number of others, can produce a latent image on the photographic plate. The action of some of these, particularly that of hydrogen peroxide, in many ways is quite

[10] Lüppo-Cramer, *Phot. Korr.*, **38**, 166 (1901); *Ateher Phot.*, **14**, 142, 151; 15, 23 (1908); *Phot. Korr.*, **45**, 297, 352 (1908); **46**, 273, 493 (1909); **47**, 128 (1910); *cf.* also Reinders, *Zeit. phys. Chem.*, **77**, 213, 256, 677 (1911).

[11] P. P. Koch and F. Schrader, *Zeit. Phy.*, **6**, 127 (1921).

[12] W. Ehlers and P. P. Koch, *Ibid.*, **3**, 169 (1920).

[13] R. Schwarz and H. Stock, *Z. anorg. Chem.*, **129**, 41 (1923).

[14] The work of R. Stronberg with the microbalance is the only work in serious disagreement with the above statement (*Z. wiss. Phot.*, **22**, 165, 176 (1923)).

[15] Chapman Jones, *Phot. Jour.*, **51**, 159 (1911).

[16] W. Scheffer, *Brit. Jour.*, **51**, 159 (1911).

[17] M. B. Hodgson, JOUR. FRANK. INST., **184**, 705 (1917).

[18] T. Svedberg, *Phot. Jour.*, **62**, 186, 310 (1922).

[19] F. C. Toy, *Phil. Mag.*, **44**, 352 (1922).

comparable with that of light.[20] Certain phenomena concerning the action of arsenite were observed by Clark [20] and are also being studied by ourselves.

(6) Clark has recently found [21] that chromic acid treatment decreases sensitivity of the plate to arsenite as well as to light.

It appears from these and other facts, therefore, that the development specks proceed from the latent image spots, which apparently consist of colloidal silver, and that these in turn proceed from pre-exposure sensitive spots in the grain, which may also consist of silver specks, possibly only a few atoms in magnitude, as we have previously indicated.[22]

Renwick considers [23] that silver formed in the emulsion-making process is in solid solution in the silver halide in a negatively charged colloidal condition and is rendered neutral by the emission of its negative charge under the influence of light. He argues this on the ground that while colloidal silver when added to the emulsion during its formation does not cause greater developability; coagulation of this by addition of acids does render the grains instantly developable without exposure.

Two of us have already suggested what we considered a more plausible explanation,[24] namely, that light releases a photo-electron from the colloidal silver speck, which we suppose to be neutral and not negatively charged [25] as supposed by Renwick. This electron then neutralizes a near-by silver ion in the AgBr lattice. The

[20] Constantin Dombrowsky, *Inaug. Dissert.*, Leipzig, 1908; T. Svedberg, *Zeit. wiss. Phot.*, **20**, 36 (1920); W. Clark, *Brit. Jour. Phot.*, **69**, 462 (1922); *Ibid.*, **70**, 762 (1923); *Phot. Jour.*, **63**, 230 (1923); S. E. Sheppard and E. P. Wightman, JOUR. FRANK. INST., **195**, 337 (1923). Only the more recent work of a quantitative nature is quoted here.

[21] W. Clark, *Brit. Jour. Phot.*, **70**, 717 (1923).

[22] Sheppard, Trivelli and Wightman, *Trans. Faraday Soc.*, **19**, 296 (1923).

[23] F. F. Renwick, *Brit. Jour. Phot.*, **70**, 382 (1923).

[24] Sheppard and Wightman, *Science*, **58**, 89 (1923).

[25] Metals like silver are considered by many physicists to consist of a lattice of atoms intermeshed with a lattice of electrons. The latter, however, are parts of the atoms, and not excess charges; they are active both in conduction and photo-electrically. In water suspension the metallic particles adsorb hydroxyl ions and hence become negatively charged. The negative charge, therefore, is not an inherent property of the colloidal condition, at least in regard to state of subdivision or dispersity. The hypothetical speck material, like other photo-electrically active material, would be effective.

freed bromide ion then also loses an electron to a neighboring Ag ion. So the chain goes on to a limiting state depending upon the initial energy of the light quantum absorbed. If this is sufficiently great then the nucleus would be large enough to initiate development for a developer of given reduction potential.

It is also possible that the bromide ion of the AgBr lattice may absorb light of certain wave-lengths, and, in the presence of a silver nucleus, give up its negative electron to the nearest silver ion in the lattice, thus enlarging the neutral silver nucleus. When this has become sufficiently large, that is, when sufficient light has acted, it also can act as a catalytic agent for the reduction of AgBr by developer. Both these effects may occur and support each other.

DESENSITIZING WITH COPPER SALTS.

Previous work on ordinary multigrain-layer high-speed plates by Mees and Sheppard [26] indicated that $CuSO_4$ merely shifted the H. and D. curve to the right, *i.e.*, lowered speed, but had no appreciable effect on gamma. Some recent tests on ordinary Graflex plates, unwashed after the $CuSO_4$ treatment, gave similar results to those of Mees and Sheppard.

The emulsion from a Seed Graflex plate was removed, diluted, and coated in one-grain layers on plate glass (5.08×12.70 cm.^{2}). One-half of each of these plates (lengthwise) was bathed in 1 per cent. ($= 0.04$ M.) $CuSO_4$ solution. Following this, the treated portions of one-half the plates were rinsed in distilled water containing 0.002 per cent. KBr, and dried. The treated portions of the other half were given a series of five washes of two minutes each in similar water, finally completely rinsed and dried. The plates were then all exposed simultaneously in a Jones Paper Sensitometer under known conditions, developed six minutes in N/10 ferrous oxalate, fixed, washed, and dried. The densities on the "blank" or untreated portions of the plates, as well as on the treated portions were determined by means of the thalofide cell densitometer [27] and the averages from ten plates are recorded in Table I. The densities are plotted against log exposure in Fig. 1.

[26] Mees and Sheppard, "Theory of the Photographic Process," p. 247.

[27] A. L. Schoen, *J. Opt. Soc. Am.*, 7, 483 (1923).

It can be seen from Table I that, contrary to the effect on ordinary plates, gamma infinity, or the slope of the normal exposure portion of the characteristic *D*-log *E* curve for complete development (the time of development was so chosen as to give approximately this), is increased by the $CuSO_4$ treatment, the maximum density remaining about the same and being produced at about the same exposure.

There was practically no difference between the rinsed and well-washed plates, and so no separate data are given for these. This may have been due to the fact that ordinary distilled water was used for washing, and that to remove the last traces of

TABLE I.

Copper Sulphate Densensitizing.

Approx. Exp. in Ergs.	Density.	
	Graflex Untreated.	Graflex Treated.
0.675	0.007	0
1.25	0.016	0.002
2.49	0.030	0.008
4.98	0.046	0.020
9.95	0.061	0.038
19.9	0.085	0.067
39.8	0.100	0.090
79.5	0.109	0.112
159.0	0.125	0.133
318.0	0.140	0.141
636.0	0.145	0.143

$CuSO_4$, an acid wash should have been used, *i.e.*, on the acid side of the iso-electric point of gelatin. This point is to be tested.

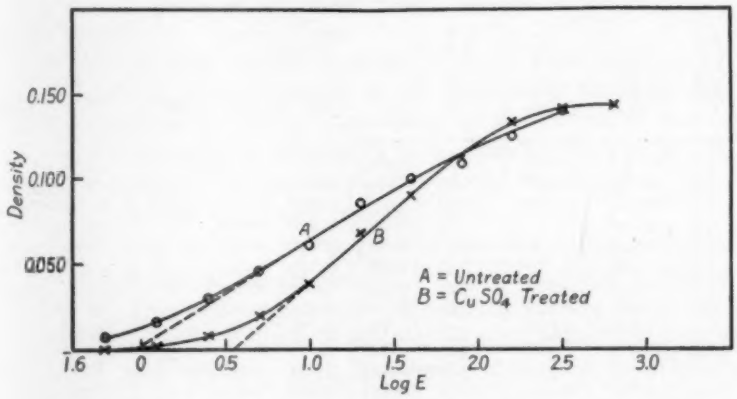
CrO_3 and $KMnO_4$ solutions both cause an increase in gamma on one-grain-layer Seed Graflex plates, but also shift the whole curve to the right along the exposure axis as well, and hence lower the sensitivity to a greater extent.

It has been supposed that the action of $CuSO_4$ is not similar to that of CrO_3 and $KMnO_4$, namely, that of an oxidizing agent acting on sensitivity nuclei, but due to adsorption retention and inhibition of photocatalysis by latent image destruction.

Mr. Bullock of this laboratory has found that in the presence of alkaline chlorides or bromides (added intentionally along with the $CuSO_4$), the sensitivity and latent image are both much more reduced than when one of these salts is not added.

Practically all photographic emulsions have at least a trace of alkaline halide present adsorbed to the grains. The excess salt is never completely washed out during their manufacture. If the previously mentioned theory of pre-exposure nuclei is correct and these nuclei consist of colloidal silver particles, then when $CuSO_4$ is added, we may have a reduction of this to cuprous salt and an oxidation of the silver nucleus to silver halide. That is to say, the same action is possible in regard to "sensitivity nuclei" as previously supposed by Mees and Sheppard in regard to the latent image by retained copper salt. The cuprous salt could then be aerially oxidized and become again effective. These matters

FIG. 1.



cannot be considered as settled, and experiments are in progress to determine the conditions of adsorption of copper ions, halide ions, silver ions, etc., and the relative adsorption densities and displacement values.

In a given emulsion, the preponderance of octahedral or cubic faces, respectively, would play a large part in this. Ag^+ ions will adsorb anions—as halogen ions, hydroxyl ions, etc.—while Br^- ions will adsorb cations—as Cu^{++}, Ag^+, etc. It is doubtful if more than a monatomic layer can be formed [28] and uncertain if the full quota thus possible of a given ionic species is adsorbed.[29] Also, while smaller grains with a larger surface per unit mass could

[28] *Cf.* K. Fajans and K. v. Beckerath, *Zeit. physik. Chem.*, **97**, 478 (1921).
[29] *Cf.* F. Paueth, *Zeit. physik. Chem.*

adsorb absolutely more than large grains (per unit mass of halide) there need be no greater adsorption density per unit surface. It is this latter factor which would affect sensitivity chiefly.[30]

CHROMIC ACID AND THE LATENT IMAGE.

When photographic plates are treated for different lengths of time with chromic acid, exposed, developed, etc., there is at first a rapid decrease in sensitivity with increasing time of treatment,

TABLE II.

Effect of Time of Treatment with 0.5 per cent. (= M/20) CrO_3 + 0.2 per cent. H_2SO_4 on Latent Image; Exp. behind Step Wedge; Dist. 200 cm.; Treated Plates 100 min. exposure; Blanks, 10 sec. exposure.

Lamp at 4V; 78 Filter.

Time of Development = 3 min. in 1:1 Pyro at 17°.

Relative Exposure.	D for Blank—No. Treat.	D for Na_2CO_3 5 per cent.	Relative Exposure.	D for CrO_3 Treatment Times. 40′	80′	120′	960′	Relative Exposure.	D for CrO_3 20′.. Exp. 960′.
1.	0.072	0.056	60	0.054	0.022	0.015	0	576	0.183
1.4	0.086	0.079	84	0.059	0.025	0.021	0	806	0.192
2.2	0.162	0.169	132	0.076	0.037	0.029	0	1270	0.238
2.9	0.199	0.203	174	0.090	0.048	0.046	0	1670	0.235
3.5	0.245	0.251	210	0.085	0.042	0.046	0	2020	0.247
4.2	0.267	0.270	252	0.086	0.049	0.037	0	2420	0.248
5.6	0.354	0.373	336	0.112	0.063	0.048	0	3230	0.268
6.6	0.407	0.405	396	0.122	0.063	0.054	0	3800	0.275
8.3	0.462	0.432	498	0.114	0.076	0.076	0	4780	0.272
10.7	0.504	0.477	642	0.122	0.076	0.061	0	6260	0.271
15.4	0.595	0.550	924	0.147	0.083	0.051	0	8870	0.285
20.9	0.666*	0.616	1254	0.147	0.068	0.069	0	12000	0.280
33.0	0.728*	0.728*	1980	0.154	0.103	0.088	0.007	19000	0.287
41.5	0.798*	0.770*	2490	0.150	0.128	0.096	0.008	23900	0.287
62.8	0.854*	0.868*	3768	0.158	0.147	0.105	0.015	36100	0.290

* Estimated from Jones Densitometer.

which then gradually approaches a constant value. It was thought to be of interest also to try such a treatment with respect to the latent image. A series of strips was therefore exposed behind a step wedge under the conditions stated at the head of Table II. On account of the very considerable destruction of the latent image by the chromic acid for exposures equal to the "blanks," it was necessary to increase the exposures of the treated plates considerably, as shown (about 600 times).

[30] This appears to have been overlooked by Germann and Hylan in their recent contentions (*J. Phys. Chem.*, **28**, 449 (1924)).

With a few exceptions, the densities were determined by means of the thalofide cell densitometer. It will be observed that the slope of the density exposure curve is much reduced by the treatment; considerable destruction of the latent image has taken place; and the destruction increases with increasing times of treatment until almost no image is developable except at the highest exposure given (which is nearly 3800 times the lowest exposure).

An endeavor was made to increase exposures enormously (36,000 times the minimum) in order to see if the densities produced on normal exposure could be reached or approached. The time of treatment was made comparatively short.

While the densities were raised somewhat the normal condition was never reached, the densities reaching the maximum value at a low density.

A question which arises in view of these experiments is, why does any latent image develop at all after such extended CrO_3 treatment, and with such a comparatively short time of development? It is apparently quite difficult to remove the last traces of the latent image. It may be equally hard, therefore, to remove the last traces of sensitivity nuclei.

Further experiments are in progress on the action of permanganate on the latent image and on the sensitivity both with and without preliminary exposures. Preliminary tests have shown that permanganate is much more active in its destruction of the sensitivity than chromic acid, and hence should be a better tool to work with.

We wish to express our thanks to Mr. A. M. Burgess for assistance in the experimental work.

Some Experiments on the Convection of Heat in Vertical Water Columns. H. H. POOLE. (*Scientific Proceedings of the Royal Dublin Society,* Vol. 17, No. 33.)—This investigation was undertaken in order to get information on the transfer of heat in the earth outward by means of convection in the water held in pores and fissures of the rocks.

A vertical glass tube contained the water under examination. Heat was supplied to its lower part by a coil traversed by an electric current. The resulting upward flow of liquid transported the heat to the top of the column, whence it was removed by a stream of cool water in a worm. The process was allowed to continue for several

hours to assure the reaching of a steady state. In that case, after allowance was made for the transfer of heat by other processes than convection, the heat imparted to the water by the heating coil was carried to the top and removed by the worm. The results are stated in terms of a new quantity. "Since it was desired to estimate the probable magnitude of the effect of convection on the thermal conductivity of the earth's crust, it appeared to be most convenient to state the result in terms of a quantity analogous to the conductivity of a solid. This quantity, which may be called the 'convectivity,' is defined as the heat flow per sq. cm. of total horizontal area per sec. divided by the gradient G." The gradient presumably means the difference in temperature between the upper and lower ends of the water divided by the vertical distance in cm. between the two levels. A second series of experiments was conducted with two vertical tubes of water side by side and with their lower ends connected. In nearly all cases the convectivity increased with an increase of the gradient. In one double tube of diameter 2.8 cm., however, for quite a range of gradient the convectivity was about proportional to this quantity. "The length of the column has also a great effect on the convectivity for a given gradient; in fact, the flow of heat up a tube of given diameter, for a given temperature difference between the ends, was generally about the same for short and long tubes, in spite of the fact that with the former the gradient was much greater." Twenty-three cm. was the length of the longest tube used.

After applying the experimental values obtained to the conditions existing in the earth's crust the author reaches the conclusion: "Thus we should expect that, in the upward flow of heat through a water-logged porous rock, convection would play a very small part. The presence of water in the pores would doubtless greatly reduce their thermal resistance and prevent the rock from acting as a very bad conductor of heat like dry pumice, but there is no reason to suppose that it would raise the effective conductivity even as high as that of an otherwise similar rock devoid of pores. On the other hand, the presence of water-filled fissures of a couple of centimetres across, or more, should add very considerably to the upward flow of heat, especially if their shapes were such as to favor continuous circulation."

G. F. S.

New Meteoric Iron.—*English Mechanics* (1924, 120, 43) reports that a French scientist has recently found in the Adriar desert in the Sahara, a variety of meteoric iron differing somewhat from the known forms. It contains about 20 per cent. of nickel. The specimen weighs several pounds, and was found near an enormous block of similar material lying in the desert. According to the report of the size of this block, it would constitute the largest mass of extra-terrestrial matter yet noted.

H. L.

SPECTROSCOPY AND BOHR'S THEORY OF ATOMIC STRUCTURE.*†

BY

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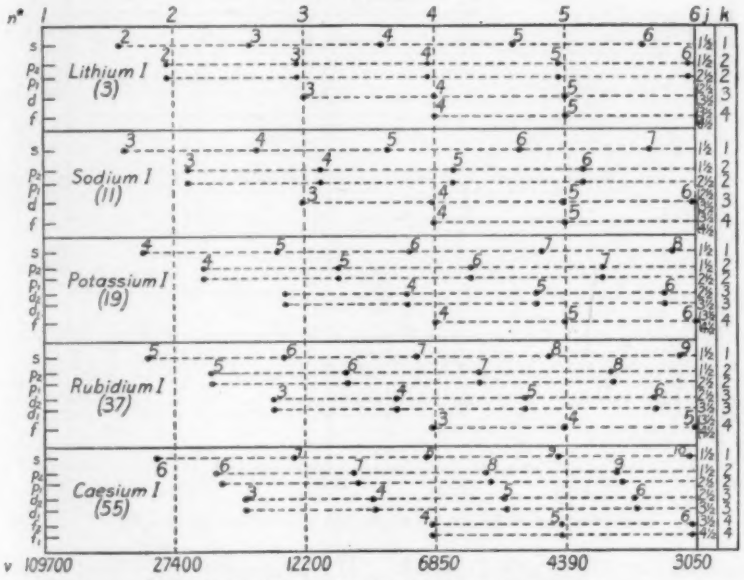
EFFECTIVE QUANTUM NUMBERS.

Fig. 5 represents graphically the effective quantum numbers for the variable terms in the arc spectra of the alkalies. The

FIG. 5.



Spectral term diagram for the arc spectra of the alkalies.

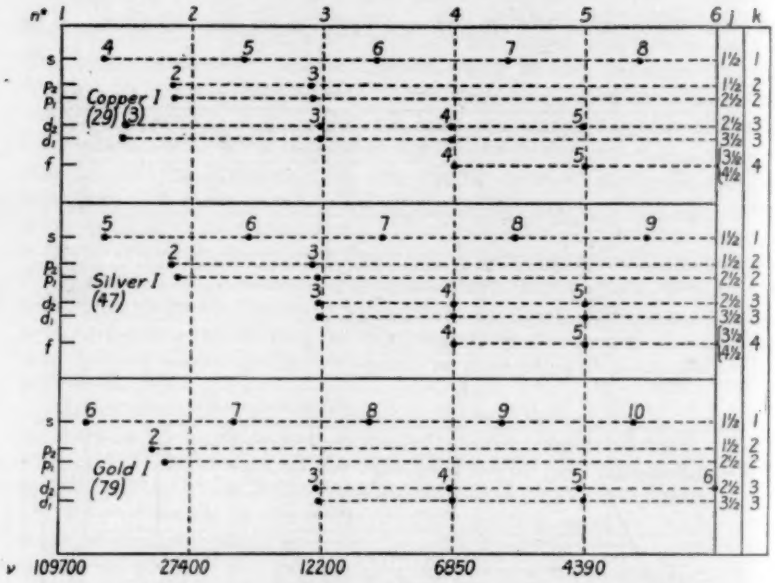
upper scale of abscissas gives the values of n^*, and the lower scale the corresponding wave numbers. The dotted vertical lines for integral values of n^* represent the hydrogenic terms $\nu = R/n^2$ so that any term in the alkali spectrum must lie to the left of the hydrogenic line for the same chief quantum number.

* Presented at a meeting of the Institute held February 14, 1924. Published by permission of the Director of the Bureau of Standards, Department of Commerce.

† Concluded from September issue, p. 363.

This value of n as assigned by Bohr is indicated by the numeral at the position of each plotted point. The large deviations of the s and p terms from the corresponding hydrogen terms, the much smaller deviations for the d terms and the practically exact agreement between the f and the corresponding hydrogen terms are readily apparent. Where the separation is large enough to be resolvable, the p, d, and f terms are found to be doublets as indi-

FIG. 6.

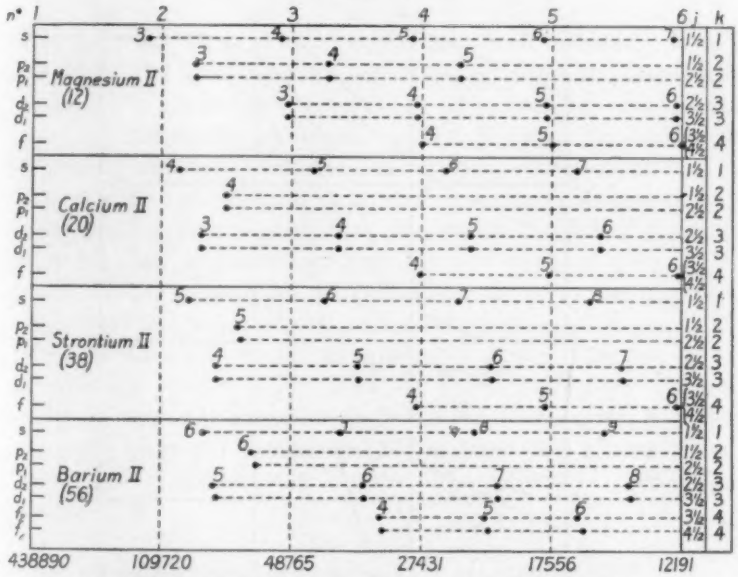


Spectral term diagram for the arc spectra of copper, silver and gold.

cated by the subscripts 1 and 2. This multiplicity of the energy levels is probably connected with a precession of the orbital plane about the invariant axis of the atom. The introduction of a second precessional frequency requires an additional quantum number j, shown on the right of the figure, the values being those assigned by Bohr. We shall not discuss this new feature of the problem in the present paper, but simply call attention to the fact that the terms which we are considering as single often possess a very complicated structure, especially for elements on the right-hand side of the periodic table. Fig. 6 shows a similar diagram for the other metals of Group I.

In Fig. 7 are plotted the values of n^* for the ionized alkaline earths computed from the formula $\nu = 4R/n^{*2}$. The values of ν for the same effective quantum number are four times those in the preceding figures since the charge on the kernel of the atom has been doubled. The vertical dotted lines correspond to the terms in the spectrum of ionized helium. The *s* and *p* terms are decidedly non-hydrogenic, the *d* terms much closer to hydrogenic

FIG. 7.



Spectral term diagram for the spark spectra of the alkaline earths.

values and the *f* terms for the lighter elements are practically equivalent to those of HeII.

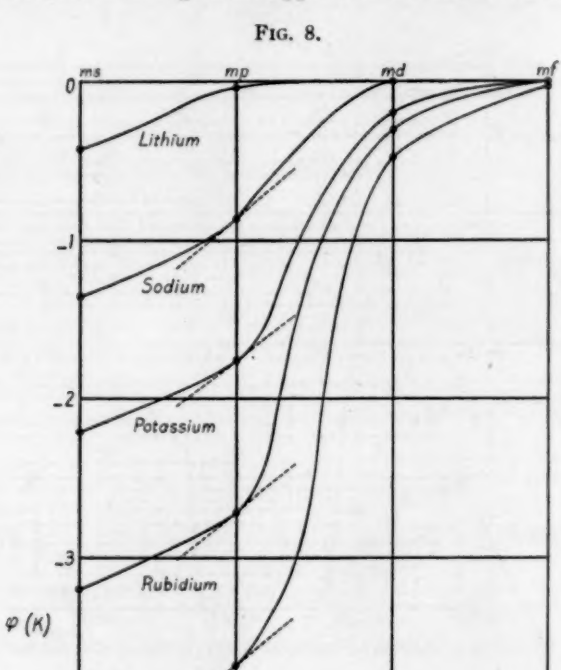
Diagrams of this character are quite useful in estimating unobserved terms in a spectrum. For example, n^* plotted against the period of an alkali gives a smooth curve. Although the corresponding terms in Fig. 5 are not quite equally spaced vertically, as they should be to illustrate the point in question, one readily sees that the relation between the same *ms* terms in the different elements is practically linear and a fairly smooth curve may be drawn for the other sequences, so that by extrapolation one may roughly estimate the terms in the unknown element ekacæsium.

Brackett and Birge [10] have pointed out relations between n^* and the number of underlying groups of electrons in the atom, which relations have been utilized in the discovery of new variable terms.

ORBITAL AND PRECESSIONAL FREQUENCY.

Equation (31) for the energy of the system with the single valence electron on an n_k orbit applies to the neutral atom, *i.e.*, to

FIG. 8.



Quantum defect for terms in the arc spectra of the alkalies.

the arc spectrum. This may be extended to any ionized atom of the alkali type as follows:

$$E = -\frac{R\,hcp^2}{[n+\varphi(k)]^2} = -\frac{R\,hcp^2}{n^{*2}} = -hcv \qquad (33)$$

[10] *J. O. S. A.* and *R. S. I.*, **8**, 213–43, 1924.

where $p = 1$ for a neutral alkali, 2 for a simply ionized, alkaline earth, etc., the factor p representing the numerical value of the net positive charge on the kernel. From equations (16) and (17) we obtain on differentiating (33)

$$\text{Orbital frequency} = \omega = \frac{2cv}{n^*}, \tag{34}$$

$$\text{Precessional frequency} = \sigma = \frac{2cv}{n^*}\frac{\partial\varphi}{\partial k}, \tag{35}$$

$$\text{Precession per revolution} = \sigma/\omega = \partial\varphi/\partial k. \tag{36}$$

Knowing n^* from spectroscopic data and assuming Bohr's values for n, the quantity $\varphi\ (k)$ in equation (33) is numerically determined. This is found empirically to be roughly independent of n, as the simple theory required, Fig. 8 shows the values of $\varphi(k)$ plotted against k for the alkali spectra. The slopes $\partial\varphi/\partial k$ of these curves for different azimuthal quantum numbers cannot be determined with any accuracy. However, the dotted tangents at $k = 2$ are fair guesses, sufficient for our purpose. Table VI gives the orbital frequencies computed directly from spectroscopic data by equation (34), and the precession per revolution, using the graphical estimates of $\partial\varphi/\partial k$ in equation (36), for the $2p_1$ terms of the alkalies. Since $\varphi\ (k)$ does not depend materially upon n, the value of $\partial\varphi/\partial k$ is constant for all terms of the same k. That is, the precession per revolution is the same for all ms terms, for which $k = 1$, and likewise for the other sequences with different values of k.

TABLE VI.

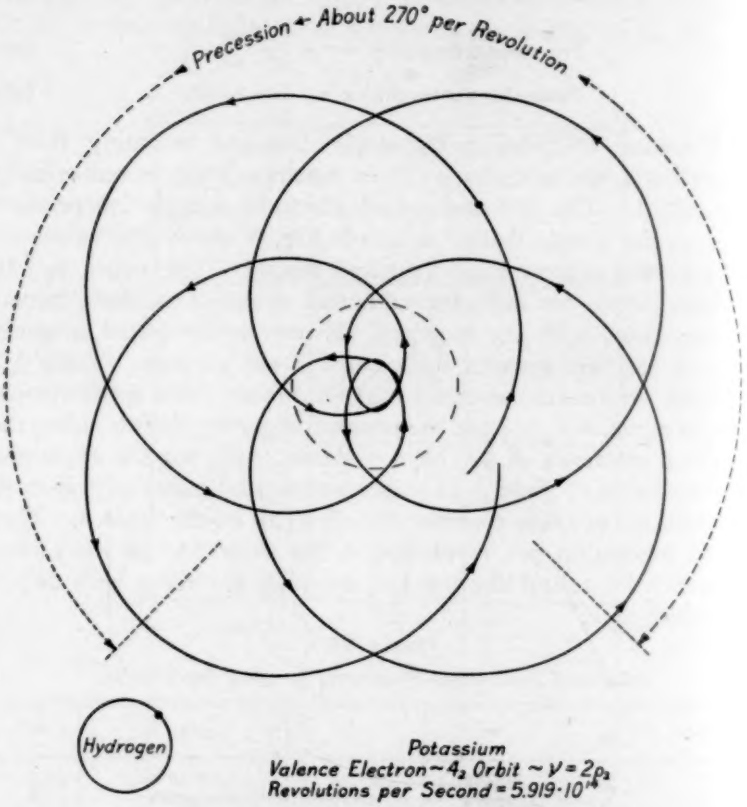
Orbital and Precessional Frequencies for $2p_1$ of the Alkalies.

Element.	n_k	ν	n^*	ω	σ/ω
Li	2_2	28581	1.959	$8.75\cdot10^{14}$	0.3
Na	3_2	24476	2.117	$6.93\cdot10^{14}$	.8
K	4_2	21963	2.235	$5.89\cdot10^{14}$	.7$_5$
Rb	5_2	20868	2.293	$5.46\cdot10^{14}$	.8
Cs	6_2	19674	2.362	$5.00\cdot10^{14}$	.8

Fig. 9 illustrates the $2p_2$ orbit and Fig. 10 the $1s$ orbit of potassium. The precession per revolution was estimated in the manner described and the orbital dimensions for the outer elliptical loops follow from equations (22) and (23). The small dotted circle represents the envelope to the orbits of the inner electrons

within which region the precession occurs. No attempt was made to represent properly the small inner loops. The scales of the drawings are indicated by the hydrogen models. If one considers that the valence electron traverses the inner loop relatively rapidly,

FIG. 9.


Precession ← About 270° per Revolution
Hydrogen
Potassium
Valence Electron ~ 4₂ Orbit ~ ν = 2ρ₂
Revolutions per Second = 5.919·10¹⁴

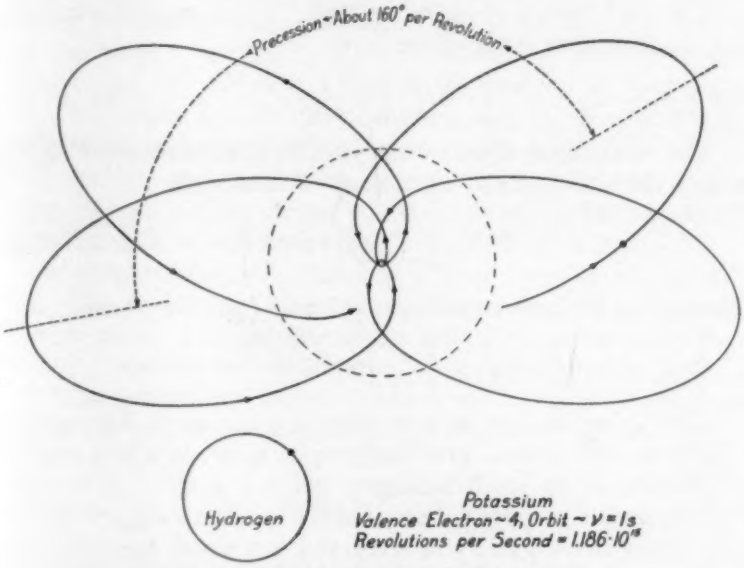
The precessing $2p_2$ orbit in potassium.

it is evident that the electron lies some distance outside the atom-kernel for by far the greater portion of time. For example, a comet in our solar system may pass around the perihelion portion of its orbits in a few days and require years to travel the outer or aphelion region. This effect is accentuated in the atomic model by the rapid increase in the effective attracting charge as the orbit penetrates the kernel.

EFFECTS OF POLARIZATION.

In the discussion of the schematic model of Fig. 3, it was assumed that the shell of charge remained rigid. Actually, however, the atom-kernel is polarized by the field of the valence electron so that it acts approximately as a doublet with the axis always pointing toward the revolving electron. Hence even though the valence electron revolves in an orbit which entirely surrounds

FIG. 10.


Precession ~ About 160° per Revolution
Hydrogen
Potassium
Valence Electron ~ 4, Orbit ~ ν = 1s
Revolutions per Second = 1.186·10¹⁵

The precessing 1s orbit in potassium.

the kernel, the field arising from the doublet slightly increases the total attractive forces above that of a hydrogenic atom with unit nuclear charge. If M is the electric moment produced on the kernel by unit field, the force on the electron due to the doublet is readily seen to be $2e^2M/r^5$. Hence the total force acting on the valence electron while outside the kernel is given by the relation

$$\text{Total force on valence electron} = \frac{e^2}{r^2}\left[1 + \frac{2M}{r^3}\right]. \qquad (37)$$

In addition to the Coulomb attraction we therefore have a perturbing force which causes orbital precession. This precession

fortunately is very small compared with that which occurs *within* the shell of charge, and in general may be neglected for the penetrating orbits. It is responsible, however, for the deviations of the encircling orbits from the corresponding ones in a hydrogenic atom, as illustrated by Table IV. This is most easily understood from a consideration of the circular orbits where the radius vector and the forces acting are constant. By the general quantum condition, the angular momentum p_φ of the revolving electron is $kh/2\pi$, part of which is due to the orbital precession.

The total energy E of the electron [11] on a large circular orbit in a neutral atom is therefore

$$E = E_P + E_K = -\frac{e^2}{r}\left[1 + \frac{M}{2r^3}\right] + \frac{1}{2mr^2}p_\varphi^2 = -hcv = -Rhc/n^{*2} \quad (38)$$

The centrifugal force of the revolving electron must exactly balance the total force of attraction. Accordingly

$$\frac{mv^2}{r} = \frac{p_\varphi^2}{mr^3} = \frac{e^2}{r^2}\left[1 + \frac{2M}{r^3}\right]. \quad (39)$$

Eliminating M from equations (38) and (39) we obtain

$$r = \frac{3}{4}\left[1 + \sqrt{1 - \frac{8}{9}\frac{k^2}{n^{*2}}}\right]a_h n^{*2} \text{ (for circular orbits).} \quad (40)$$

Very often, as can be seen from Figs. 5 to 7, the value of k for a circular orbit is practically equal to n^*, in which case the polarization is of small influence and $r \sim a_h n^{*2}$. Even when the polarization is quite pronounced the relation $r = a_h n^{*2}$ for circular orbits is not greatly in error and is a closer approximation to equation (40) than the relation $r = a_h k^2$, which holds for hydrogenic orbits since the parameter and radius of a circle are identical.

Since n^{*2} by definition is equal to R/ν for the arc spectrum,

[11] We assume here that the work required to remove the electron is $-E$. If the atom-kernel actually consisted of a nucleus and uniform shell of charge, this assumption would be strictly correct since the energy of such a configuration is not altered by polarization. Actually, however, one might expect that the polarizing of the kernel should require an expenditure of work, in which case the introduction of ν in equation (38) is merely an approximation. We have also assumed that the electron actually possesses the angular momentum $kh/2\pi$, whereas it might be expected that this should be shared with the kernel, as is known to be the case in a hydrogenic atom if the motion of the nucleus is considered.

it is apparent from equation (40) that k^2/n^{*2} can not exceed $9/8 = 1.13$ for a circular orbit, as it leads to imaginary values of r. When spectroscopic terms occur where $k^2/n^{*2} > 1.13$, it suggests that either the orbit is not a circle or the polarizing effect has become so strong that the revolving electron has been drawn into the kernel under which condition equation (40) is no longer applicable.

It is of interest that if equations (38) and (39) are solved for M, using the empirical spectroscopic terms of lithium corresponding to circular orbits, M, which should be constant, ranges about the value $3 \cdot 10^{-25}$ cm.^{3}. This is the electric moment of the lithium kernel for unit field. The electric moment of the helium atom, which resembles the lithium kernel, may be computed from measurement of the dielectric constant of the gas. One obtains $2 \cdot 10^{-25}$ cm.^{3}, a slightly smaller instead of an anticipated larger value (since the nuclear charge is less for helium), but we should be satisfied with an agreement merely in order of magnitude.

One may consider the polarization effect from another standpoint. The perturbing force of polarization produces a precessional frequency σ in addition to the orbital frequency ω, so that the total frequency of the electron on a large circular orbit is $\omega + \sigma$. On putting the angular momentum equal to $kh/2\pi$ and equating the centrifugal and attracting forces, we obtain

$$r^2 = \frac{kh}{4\pi^2 m(\omega + \sigma)}. \tag{41}$$

Making use of equations (33) to (35), this reduces to

$$r = a_h \sqrt{\frac{n^{*3}k}{1 + \partial\varphi/\partial k}} \tag{42}$$

for a neutral atom, where $\partial\varphi/\partial k$ may be roughly estimated from spectroscopic data in the manner already described. Table VII gives in terms of a_h, the radii of the various circular orbits concerned with the arc spectra of the alkalies, as computed by the preceding formulas.

The values in the last column are unsatisfactory because $\partial\varphi/\partial k$ cannot be determined from the curves of Fig. 8 with sufficient precision. In fact, one might better compute the radii by equation (40) and evaluate $\partial\varphi/\partial k$ through equation (42). For the $3d$

TABLE VII.

Large Circular Orbits for the Alkalies.

Element.	Term.	n_k	n^*	$\frac{\partial\varphi}{\partial k}$	k^2a_k	Radius Computed by Different Formulas.		
						$n^{*2}a_k$	Eq. (40).	Eq. (42).
Li	$2p$	2_2	1.959	.3	$4a_k$	$3.84a_k$	$3.66a_k$	$3.4a_k$
	$3d$	3_3	2.999	.3	9	8.99	8.99	7.9
	$4f$	4_4	4.000	0	16	16.00	16.00	16.
Na	$3d$	3_3	2.989	.6	9	8.93	8.87	7.1
	$4f$	4_4	3.992	.1	16	15.94	15.87	15.
K	$3d$	3_3	2.854	.8	9	8.15	6.93	6.2
	$4f$	4_4	3.994	.1	16	15.95	15.90	15.
Rb	$3d$	3_3	2.767	.8	9	7.66	?	5.9
	$4f$	4_4	3.990	.2	16	15.92	15.84	15.
Cs	$3d$	3_3	2.549	.9	9	6.50	?	5.1
	$4f$	4_4	3.978	.3	16	15.82	15.64	14.

terms of Rb and Cs we find $k^2/n^{*2} > 9/8$, which suggests that the orbits are ellipses instead of circles as assumed by Bohr.[12]

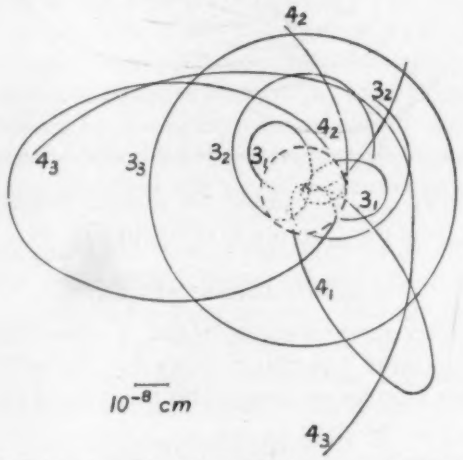
[12] It is questionable if these could be deep-lying circular orbits since the ion radii are, according to Davey (*Phys. Rev.*, **22**, 211, 1923), but little greater than the radius of K^+. Davey's crystal measurements are $K^+ = 1.548$ Å., $Rb^+ = 1.679$ A. and $Cs^+ = 1.974$ Å. From entirely different reasoning Brackett and Birge (*loc. cit.*) have assigned the quantum numbers 4_3 and 5_3 to the $3d$ terms of Rb and Cs, respectively, thus making the orbits elliptical. These assignments are in agreement with Bohr's for the $3d$ terms in the spark spectra of the next following elements, Sr^+ and Ba^+, as shown in Fig. 7. They are furthermore indicative of the initiation of the development of the underlying shell in succeeding elements. For example, with these assignments we have the following data:

n_k	Term.	n^*	
		K	Ca^+
4_1	$1s$	1.771	2.141
3_3	$3d$	2.854	2.314
		Rb	Sr^+
5_1	$1s$	1.805	2.223
4_3	$3d$	2.767	2.435
		Cs	Ba^+
6_1	$1s$	1.869	2.333
5_3	$3d$	2.549	2.420

SCHEMATIC REPRESENTATIONS OF OPTICAL ORBITS.

If the valence electron in an atom of the alkali type, on the various penetrating optical orbits which it may occupy, reaches such a large aphelion distance that the effect of polarization is relatively small, the outer loop of the orbit is approximately a non-precessing Keplerian ellipse with the semi-major axis $a = a_h n^{*2}$ and semi-minor axis $b = ak/n^*$, most of the precession taking place within the atom-kernel. The radius of a circular orbit which surrounds the kernel is also given approximately by

FIG. 11.



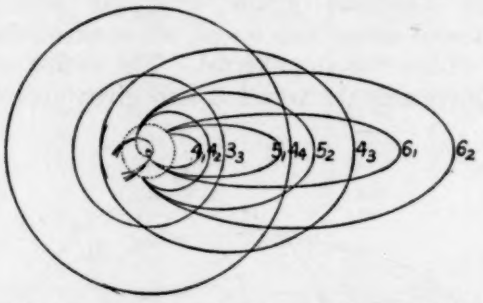
Optical orbits in sodium (reproduced from "Bohr's Atomteori," Holst and Kramers).

$r = a = a_h n^{*2}$ even if the polarization is considerable, but still is not sufficient to draw the electron into the kernel. Under these circumstances the orbits corresponding to the various optical terms may be readily represented graphically. Fig. 11 shows the optical orbits of Na and Fig. 12 those of K. The size of the atom-kernel

The values of n^* show that the nineteenth electron is tending to become relatively more firmly bound in a $3d$ orbit as the atomic number increases, which by extrapolation indicates that the *highest* term in the, at present, unknown spectrum of Sc^{++} should be $3d$. That is the nineteenth electron in the building of Sc, and from similar reasoning, the thirty-seventh electron in Y and the fifty-fifth electron in La revolve in $3d$ orbits with the quantum numbers 3_3, 4_3, 5_3, respectively, which is consistent with the data of Fig. 4. This reasoning, however, is so obvious that possibly Bohr has more important evidence to the contrary.

is indicated by a dotted circle. All penetrating orbits of the same azimuthal quantum number "precess" on the inner loop in a similar manner as shown. The various lines of the arc spectrum are emitted when the electron disappears from one orbit and

FIG. 12.



Optical orbits in potassium (reproduced from Bohr's Nobel Prize Address).

appears in another. For example, the sodium D-lines correspond to a transition from the 3_2 to the 3_1 orbits in Fig. 11.

RADII OF ALKALI ATOMS.

From the preceding paragraph and a consideration of the geometry of the ellipse it readily follows that the aphelion distance r_a of the valence electron on an n_k orbit is given by the relation

$$r_a = a_h n^{*2}\left[1 + \sqrt{1 - \frac{k^2 a}{n^{*2}}}\right] \qquad (43)$$

TABLE VIII.

Diameter of Alkali Atoms.

Element.	1s orbit.		r_a	Diameter of Atom.	Shortest Distance between Atom Centres.	References.
	n^*	n_k				
Li	1.589	2_1	$4.487a_h$	4.75 Å.	3.02 Å.	Bijvoet and Karssen
Na	1.627	3_1	4.735	5.01	3.71	Hull
K	1.771	4_1	5.723	6.05	4.50	McKeehan
Rb	1.805	5_1	5.972	6.32	4.93	Computed from density assuming same manner of packing (body-centred cubic).
Cs	1.869	6_1	6.445	6.82	5.31	

In the normal state the valence electron revolves on a $1s$ orbit for the alkalies so that $k = 1$. The values of r_a thus computed from spectroscopic data on n^* are given in Table VIII.

We have seen from Fig. 10 that these orbits are rapidly precessing and, as has been mentioned, there is also a precession of the orbital plane itself, a discussion of which could not be incorporated in the present paper. On account of these precessions the aphelion distance describes a surface of revolution which may be roughly considered a sphere of radius r_a. The diameter of the isolated atom is therefore $2r_a$, as given in column 5, where, recalling that $a_h = 5.29 \cdot 10^{-9}$ cm., the values are expressed in Ångström units (10^{-8}cm.). These magnitudes apply for the atoms in the vapor state. The distances between centres of adjacent atoms in the crystalline state of the solid metal may be accurately determined by X-ray crystal analysis, or may be computed from the density when the manner of packing is known. The shortest distance between the atoms, observed in this manner, is given in column 6. It is therefore evident that in the solid state the atoms are packed so closely that the valence electron does not have sufficient space to revolve in the normal $1s$ orbit characteristic of the element in the gaseous state. All the optical orbits are suppressed in the solid so that the alkalies are unable to emit their arc spectra when bombarded by electrons. The packing, however, is not so close as to interfere with the deeper underlying shells so that the X-ray spectra, except possibly the softest X-rays, are unaffected. In the solid state the valence electrons are simultaneously in the field of several atoms. No doubt they drift about through the lattice structure and possess the general characteristics of free electrons, the conception of which has led to a more or less satisfactory interpretation of the main phenomena of conduction and dispersion in metals.

DEVIATIONS OF SPECTRAL TERMS FROM THE RYDBERG TYPE.

In the preceding discussion we have assumed that the spectroscopic terms could be represented by the Rydberg formula, equations (21) and (32), where φ is a constant for all the terms belonging to any particular sequence. While this is frequently true with a high degree of approximation, variations of considerable interest occur, as illustrated by Table IX, in which are listed the empirical values of φ for the terms in the potassium spectrum.

TABLE IX.

Value of $-\varphi$ in Rydberg Formula (Potassium).

n	s	p_1	d	f
3	—	—	.146	—
4	2.220	1.765	.203	.006
5	2.198	1.734	.229	.009
6	2.189	1.723	.243	.009
7	2.185	1.717	.251	.009
8	2.182	1.716	.259	
9	2.179	1.712	.257	

The *numerical* value of φ decreases with increasing n for the s and p sequences, which, as we have already seen, correspond to orbits that penetrate into the kernel. The variation of φ with n is in the opposite direction for the d and f sequences which correspond to orbits lying outside the kernel. These types of variation are quite general. Since $\varphi = 0$ for a hydrogenic atom, the s and p terms *tend* to become more closely hydrogenic and the d and f terms less closely hydrogenic with increasing chief quantum number, although for any value of n the approximation to hydrogenic conditions is always closest for the f terms and least for the s terms, as shown by the actual deviations of φ from zero. While this is best understood after rather complete mathematical analysis, it may be explained sufficiently for our purpose by qualitative reasoning.

It will be noted from an examination of Fig. 2 that in a hydrogenic atom the perihelion distance r_p for a family of orbits having the same value of k decreases as n increases. From simple geometry one finds

$$r_p = a_h \left[1 - \sqrt{1 - k^2/n^2}\right] \frac{n^2}{Z} \qquad (44)$$

For the orbits in hydrogen of azimuthal quantum numbers $k = 3$ and 4 the perihelion distances are as given in Table X.

Thus as n increases, the perihelion distance decreases, approaching a limit value equal to half the radius of the circular orbit for the same azimuthal quantum number.

In a non-hydrogenic atom, for terms corresponding to orbits which surround the kernel, the relations are qualitatively similar. However, on account of the polarization effect, which varies extremely rapidly as the electron approaches the kernel, there is

a strengthening in the binding of the revolving electron which increases the closer the perihelion lies outside the kernel. The terms therefore become less hydrogenic as the chief quantum number increases, but the *rate* at which they become less hydrogenic decreases since the value of r_p approaches a minimum asymptoti-

TABLE X.

Perihelion Distances for Orbits in Hydrogen.

n_k	r_p	n_k	r_p
3_3	$9.00a_h$	4_4	$16.00a_h$
4_3	5.42	5_4	10.00
5_3	5.00	6_4	9.17
6_3	4.82	7_4	8.79
7_3	4.73	8_4	8.58
.	.	.	.
.	.	.	.
.	.	.	.
∞_3	4.50	∞_4	8.00

cally. Such a condition is illustrated by the numerical increase in φ with n for the d and f sequences in potassium (Table IX) and in the other alkalies.

That the relations should be just the opposite for the penetrating orbits is not so apparent. It may be shown mathematically, however, on the assumption of a model such as illustrated by Fig. 3, or with models of a much more general character, that the inner loops are practically identical [13] for all penetrating orbits having the same azimuthal quantum number, regardless of the value of n. If the inner loops were exactly alike, the *differences* in the strengths of binding of the various orbits having the same k would be due entirely to changes in the outer loops. The aphelion distance for the outer loop increases with the chief quantum number being roughly proportional to n^2 (or more precisely n^{*2}). On account of the polarization effect, the greater the aphelion distance the closer is the approximation to a Coulomb field, and the more nearly hydrogenic the terms become. Hence for penetrating orbits the absolute numerical value of φ should decrease with increasing n, as illustrated by Table IX for the s and p terms of potassium.

[13] Wentzel, *ZS. f. Physik.*, **19**, 59, 1923. Bohr, *Ann. d. Physik.*, **71**, 259, 1923. See also the papers, *loc. cit.* of Schrödinger, Van Urk and Fues.

This deviation of terms from the Rydberg type may be illustrated in an entirely different manner. Through the recent work of Paschen and of Fowler we know the terms corresponding to the binding of the eleventh electron in Na, Mg^{+}, Al^{++}, and Si^{+++}, that is, the spectra have been correlated in series for NaI, MgII, AlIII, and SiIV. The variable terms are given by the relation $\nu = p^2 R/(n+\varphi)^2$ where p, the net kernel charge, has the values 1, 2, 3 and 4, respectively. The d and f orbits which surround the kernel are drawn closer to it as the net charge on the kernel increases. Accordingly the binding strength increases at a more rapid rate than would occur in hydrogenic fields, and the corresponding terms become less hydrogenic as the kernel charge increases. The numerical value of φ for the d and f terms of the same quantum number should therefore increase in passing from NaI to SiIV. For the penetrating orbits, corresponding to the s and p sequences, the difference between the attractive forces outside and within the kernel decreases as the net kernel charge increases. The field inside more nearly corresponds to the field outside, which is the condition for a closer approach toward the hydrogenic terms. Consequently the numerical value of φ for the s and p terms decreases in passing from NaI to SiIV. These relations are clearly illustrated by Table XI, which gives the values of φ for the first term in each sequence. A similar condition obtains for all the other terms and, indeed, the variation is so regular that one may roughly estimate terms corresponding to the binding of the eleventh electron in the following elements P and S.

TABLE XI.

Values of φ for NaI, MgII, AlIII and SiIV.

Spectrum.	Quantum defect $= -\varphi$			
	$1s$	$2p_1$	$3d$	$4f$
NaI	1.3733	.8832	.01098	.001596
MgII	1.0980	.7349	.03123	.003485
AlIII	.9258	.6301	.05074	.004315
SiIV	.8047	.5501	.06496	.004456

It is readily apparent that sequences might occur where the first few terms correspond to orbits which surround the kernel and subsequent terms to penetrating orbits. For example, sup-

pose that the kernel, represented for convenience as a rigid spherical shell, had a radius 5.2 a_h. Referring to Table X, one sees that the 3_3 and 4_3 orbits should lie outside the kernel while all n_3 orbits for which $n > 4$ should penetrate the shell. The first two terms in the d sequence therefore should be hydrogenic, or if polarization is considered, should obey approximately the Rydberg formula with a small value of φ. Succeeding d terms, corresponding to penetrating orbits, should depart considerably from the hydrogenic state so that φ should show a sharp break as the shell is entered. We accordingly have irregular or broken sequences which have been recently investigated by Wentzel.[14] These broken series, quite frequently observed, throw considerable light upon the interpretation of atomic structure. For example, the P sequence of Hg has the following successive values of $-\varphi$: .09, .08, .13, .48, .90, .98, 1.00, 1.01, etc. The sequence starts out approximately hydrogenic while higher terms have a quantum defect of about unity. There is a rapid break in the series between the third and sixth terms which indicates the beginning of the penetration into the structure of the Hg^{++} ion. Wentzel concludes from more thorough analysis that the radius of this ion is about 1 Ångström. For many other examples of interest, his original paper should be consulted.

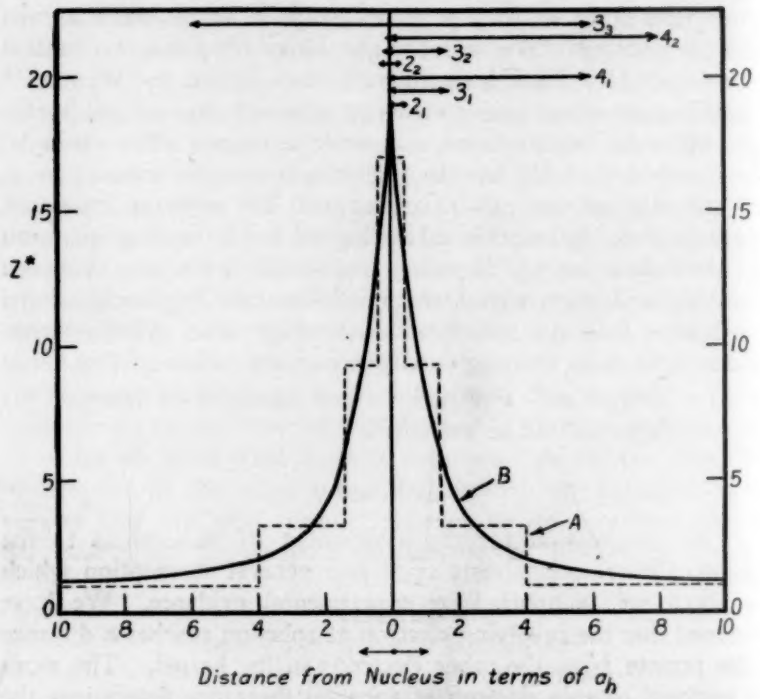
X-RAY ORBITS.

The justification for the assignment of dimensions to the various optical orbits rests upon one general assumption which has been well supported by experimental evidence. We have assumed that the revolving electron at aphelion reaches a distance quite remote from the other electrons in the kernel. The work of removal of this electron at aphelion therefore determines the total energy of the electron at that point on its orbit. The energy is of course not constant throughout the orbit. When the electron penetrates into the kernel it produces a screening action for all other electrons so that their binding strengths are reduced while the valence electron is within the kernel. There is a periodic interchange of energy between the kernel and the revolving electron. Experiment shows that it requires a definite amount of work to remove any particular electron, presumably, or possibly,

[14] Wentzel, *ZS. f. Physik.*, **19**, 53–66, 1923.

regardless of what position on the orbit is occupied at the instant of removal. It is the difference in energies of the atom before and after ionization, and not the energy of the electron removed, which determines the work of removal. If the valence electron is ejected from the atom at the instant it reaches perihelion, the resulting increase in the strength of binding of all the other elec-

FIG. 13.



The effective charge at various distances from the nucleus in the potassium atom. The projections of several orbits are shown at the top of the diagram.

trons assists in the process of removal. Hence in order to calculate the energy of the electron at perihelion it is necessary to investigate its screening action on the other electrons. If the screening effect is negligible, as is the case when the valence electron is far outside the kernel, removal of the electron at that instant produces no rearrangement in the rest of the structure, and for this portion of the orbit only, the work of ionization $= -E$, from which the orbital dimensions for that region may be obtained.

A knowledge of the works of ionization, however, is not suf-

ficient to permit an estimation of the dimensions of an X-ray orbit in the interior of the atom or the dimensions of an outer orbit when several of the same type are present, as in the outer shell of a rare gas. Even if such an electron is removed from its *aphelion* position, it is necessary to know the law governing the field of force, which may differ greatly from a Coulomb field, and the change in energy resulting from an increase in the binding of all the other electrons in the atom, especially those in orbits of the same or greater quantum number. An illuminating example is furnished by a qualitative consideration of the K-shell, where, according to Bohr, each of the two electrons present revolves in a 1_1 orbit. Each electron, therefore, has the angular momentum $h/2\pi$, and if we assume that the perturbing force of the second electron does not greatly alter the velocity of the first—an approximation which should be better the heavier the element—we obtain

$$E_K = \frac{1}{2} mv^2 = \frac{p_\varphi^2}{2mr^2} = \frac{h^2}{8\pi^2 mr^2} = \text{kinetic energy of one electron.} \quad (45)$$

The fact that there is but one ionization potential for neutral helium, and one K absorption limit for each element, indicates that the two K electrons are similarly bound to the nucleus. Hence the kinetic energy of both electrons is twice that given by equation (45), and by Burger's theorem [15] the total energy E_1 of both electrons is equal to the negative of the total kinetic energy so that

$$E_1 = -\frac{h^2}{4\pi^2 mr^2} = \text{total energy of both } K \text{ electrons.} \quad (46)$$

With a fair degree of approximation we may neglect the shielding action of the electrons in the higher shells upon the K electrons since these are within the K-shell for a very small fraction of the time. We have then,

$$E_2 = -Z^2 Rhc = \text{total energy of } K\text{-shell with one electron removed.} \quad (47)$$

The work required to remove this electron is $hc\nu$, where ν is the wave number of the K absorption limit; accordingly,

$$hc\nu = hcR\frac{\nu}{R} = -Z^2 Rhc + \frac{h^2}{4\pi^2 mr^2} - \Delta B. \quad (48)$$

The first two terms on the right represent the work done on the K-shell and ΔB is the work which the electrons in the outer shells contribute to the ejection of the K electron by virtue of the fact

[15] *Cf.* Sommerfeld, "Atomic Structure," Vieweg, 3rd ed., p. 665.

that after the removal of the inner electron, they are more firmly bound. By equation (48),

$$r = \frac{a_h\sqrt{2}}{\sqrt{Z^2 + \frac{\nu}{R} + \frac{\Delta B}{Rhc}}}. \tag{49}$$

Bohr and Coster [16] have derived a relation by which ΔB may be roughly computed. We shall, however, consider another method for estimating this quantity. After a K electron, close to the nucleus, is removed, the effective nuclear charge is increased approximately by unity for all the electrons in the outer shells. Hence ΔB is practically equivalent to the summation of the change in the work of removal of each outer electron when the atomic number of the element is increased by unity. More strictly one should compare the X-ray and optical limits of the element of atomic number Z with the corresponding limits for an element of atomic number $Z + 1$ from which a valence electron has been removed—a refinement of not much consequence.

Accordingly,

$$\Delta B = \Sigma A_i hc \Delta \nu_i = hcR\Sigma A_i \Delta\left(\frac{\nu_i}{R}\right) \tag{50}$$

where A_i is the number of electrons in the ith group, $\Delta\left(\frac{\nu_i}{R}\right)$ the change in ν/R on passing to the next element, and the summation is taken for all types of orbit of higher quantum number. Hence

$$\text{Radius of } K\text{-shell} = r = \frac{a_h\sqrt{2}}{\sqrt{Z^2 + \frac{\nu}{R} + \Sigma A_i \Delta\left(\frac{\nu_i}{R}\right)}} \tag{51}$$

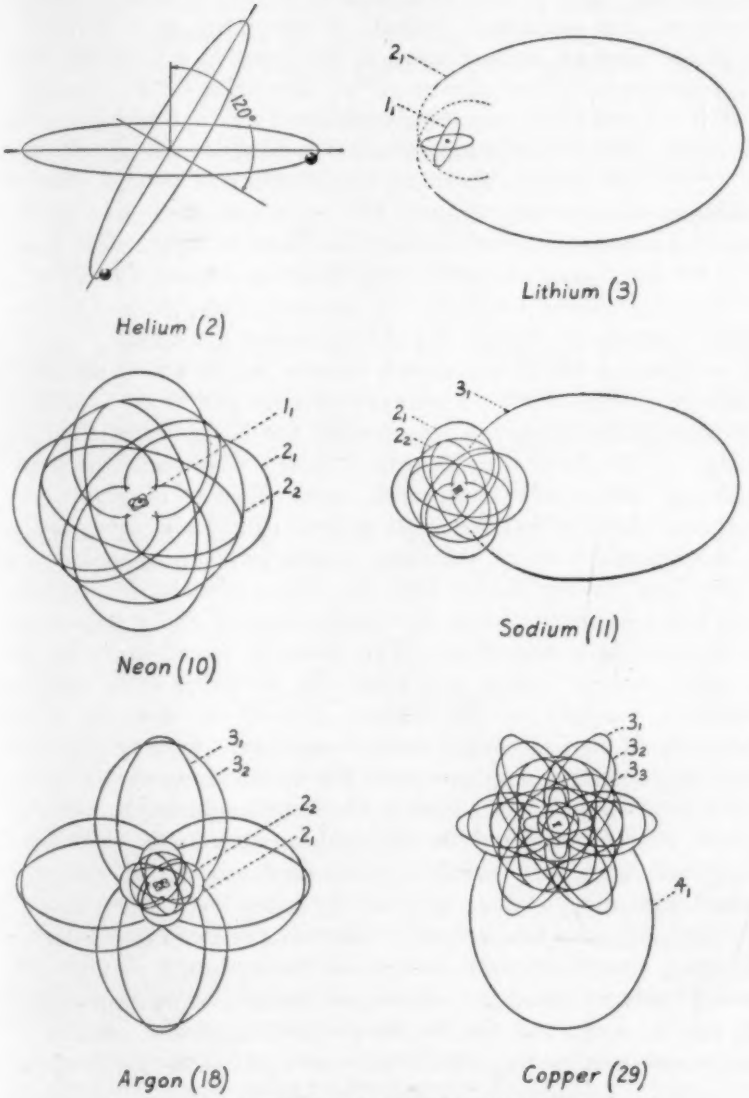
This relation may be readily evaluated from tables of X-ray limits. The assumptions upon which equation (51) is derived are of course questionable, even as approximations, and more questionable assumptions must be introduced if an attempt is made to determine the sizes of the inner orbits of higher quantum number.

Hartree[17] has recently considered the problem from a more general standpoint and has attempted to evaluate all the orbits in a complicated atom. We know that the field of force through which *any particular electron moves within its atom* actually must be of a very complicated nature. However, if we assume

[16] Bohr and Coster, *ZS. f. Physik.*, **12**, 359, 1923.

[17] Hartree, *Proc. Camb. Phil. Soc.*, **21**, 625–41, 1923.

FIG. 14.



Schematic representation of atomic models (Bohr).

that on the average the perturbing forces of the various other electrons act symmetrically, giving a net force of a central character, we may think of the total nuclear attraction and perturbing forces on one particular electron of the atom, at a distance r from the nucleus, as equivalent to the force in a Coulomb field with the single nuclear charge $+Z^*e$. The value of Z^* is a function of r, approaching the atomic number Z as $r \doteq 0$, and approaching unity, for a neutral atom, as $r \doteq \infty$. Suppose the contribution to Z^* by the various electrons in the different groups may be averaged out into contributions from spherical shells of negative charge (volume distribution might be closer to fact). The quantity Z^* is constant between such shells as shown by curve A of Fig. 13. Since, however, the various groups do not act precisely as shells of charge, one should expect the actual Z^* curve to be rounded off in some such manner as shown by curve B, which represents Hartree's computations for potassium. Making the assumption, known to be incorrect for X-ray terms, that the energy of the electron in its orbit is $-h\nu$, where ν is the corresponding absorption limit, and, using Bohr's assignment of quantum numbers and the usual quantum integrals, it is possible to determine $Z^* = f(r)$ such that it best satisfies all optical and X-ray data. When this is done (*cf.* Fig. 13, curve B for potassium), the geometrical and time characteristics of the orbits may be obtained by computation. The orbits so found resemble precessing ellipses. Table XII gives the perihelion and aphelion distances, computed in this manner, for all the electrons in the potassium atom, including the more important optical orbits which the valence electron may occupy. The first column shows Bohr's assignment of quantum numbers, the second column the observed values of ν/R, except those enclosed in parentheses, which are computed since they refer to soft X-rays lying in an unexplored region.[18]

The perihelion and aphelion distances are expressed in terms of $a_h = 5.29 \cdot 10^{-9}$ cm., the radius of the hydrogen atom. The seventh column gives the aphelion distances, or radii of circular orbits, computed by the simple considerations outlined in the present article, using the formula indicated in the final column.

[18] Mohler and the writer's work on critical potentials indicates that $M_{III} = 1.4$; while Mohler, from a consideration of all data on soft X-rays, estimates $L_1 = 27.8$ and believes that M_1 is nearer 5 than 2.4. All the other values used by Hartree are certain to the accuracy given.

The agreement with Hartree's computations is surprisingly good.

Data of this character, extended by further computations, are sufficient for the schematic representation of atomic models in which the orientations of the various orbits in space are not considered. Figs. 14 and 15 show several diagrams of this type,

TABLE XII.

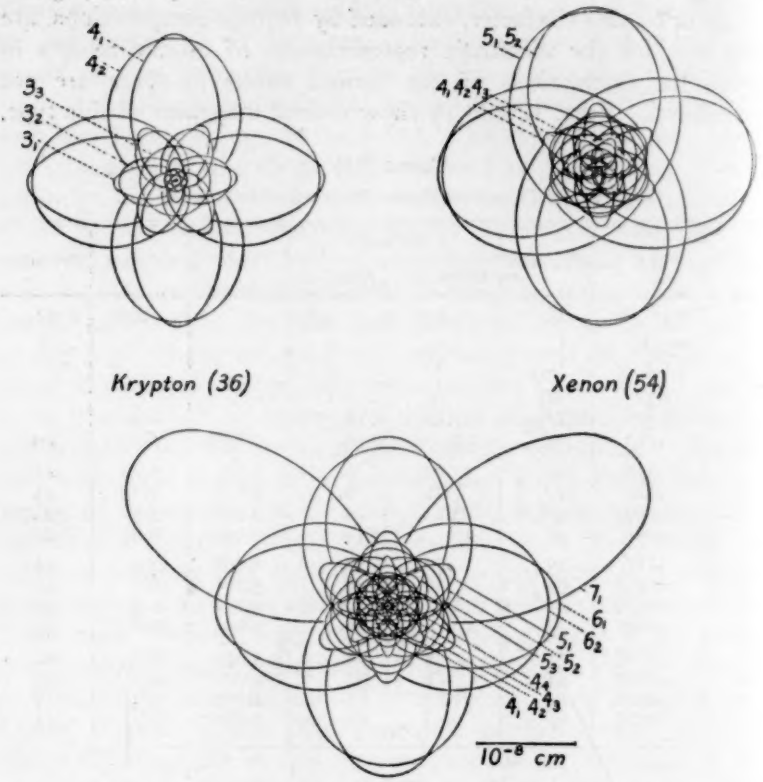
Orbits in the Potassium Atom (Dimensions in terms of a_H).

Orbit.	ν/R	Notation.	r (Hartree).		n^*	Aphelion.	Formula.
			Perihelion.	Aphelion.			
1_1	265	K	.055	.055		.056	51
2_1	(23.5)	L_I	.03	.5			
2_2	21.3	L_{III}	.3	.3			
3_1	(2.4)	M_I	.03	1.8			
3_2	(1.5)	M_{III}	.17	1.75			
3_3	.123	$3d$	6.	6.	2.854	6.93	40
4_1	.319	$1s$	.03	6.	1.771	5.72	44
4_2	.200	$2p$	.16	8.	2.235	7.23	44
4_3	.0693	$4d$	3.1	23.	3.797	23.3	44
4_4	.0627	$4f$	16.	16.	3.994	15.9	40
5_1	.127	$2s$	.03	15.	2.802	15.2	44
5_2	.0938	$3p$	.16	19.	3.266	19.1	44
5_3	.0439	$5d$	2.9	40.	4.771	40.5	44
5_4	.0401	$5f$	10.	40.	4.991	39.8	44
6_1	.0688	$3s$	.03	28.	3.811	28.5	44
6_2	.0547	$4p$	.16	34.	4.277	34.5	44
6_3	.0302	$6d$	2.7	61.	5.757	61.4	44
6_4	.0279	$6f$	9.	63.	5.991	62.7	44

originally prepared by Bohr [19] from considerations of the same general nature as those already described. Suggestions for space orientation undoubtedly may be furnished by a thorough understanding of the fine structure of spectral and X-ray lines and by interpretation of the influence of electric and magnetic fields, subjects upon which progress is being made. Aside from space configuration, however, the models, except for the optical orbits, are based on questionable assumptions, even from the quantum theory standpoint. They are merely qualitative attempts to describe an n-body problem where mathematics is incapable of any treatment whatever. On the other hand, these pictures help in visualizing some of the experimental phenomena of physics, and already very interesting relations have been discovered between the chemical behavior of an atom and its geometrical

[19] From a paper by Kramers, "Die Naturwissenschaften," 11, p. 554, 1923.

FIG. 15.



Schematic representation of atomic models (Bohr).

dimensions, or those of its ion, as estimated by the use of spectroscopic data. It appears that a real understanding of the mysteries of chemical valence may develop from the work of the empirical spectroscopist.

In conclusion the writer desires to express his appreciation for the suggestions made by Prof. C. A. Skinner and Prof. J. H. Van Vleck during the preparation of the manuscript.[20]

[20] Since this article was written a very interesting paper on "The Atomic Models of the Alkali Metals," by Doctor Lindsay, has appeared in *J. Math. Physics* (3, 191–236, 1924). Diagrams of the various orbits and the methods and assumptions employed for their computation are discussed in detail.

NOTES FROM THE U. S. BUREAU OF STANDARDS.*

SPECTRA AND CRITICAL POTENTIALS OF FIFTH GROUP ELEMENTS.[1]

By Arthur E. Ruark, F. L. Mohler, Paul D. Foote and R. L. Chenault.

[ABSTRACT.]

THE critical potentials of the nitrogen group are as follows:

Element.	Inelastic Collision Potentials.	Ionization Potential.
N	8.18 ± 0.1	16.9 ± 0.5
P	5.80 ± 0.1	13.3 ± 0.5
As	4.69 ± 0.1	11.54 ± 0.5
Sb	1.7 ± 0.5	
	5.7 ± 0.5	8.5 ± 1.0
Bi	1.9 ± 0.1	8.0 ± 0.5
	3.9 ± 0.1	
	5.7 ± 0.1	

The values for Sb are provisional; in As and Bi the potentials listed are those of the atom; the same is probably true for Sb. The resonance potentials of neutral As and Bi correspond to the mean excitation voltages of groups of spectral lines. The spectrum of the thermionic discharge in Bi was studied at potentials ranging from 4 to 60 volts. Groups of spark lines appear at 14 ± 1, 25 ± 5, and possibly at 45 ± 5 volts. These have been measured and listed according to the voltages at which they appear. No bands characteristic of the molecules of As, Sb, and Bi are found in the spectrum of the thermionic discharge. The absorption spectrum of Bi shows the lines 3067, 2276, 2230-28, 1959, and 1954 Å., and bands in the region from 2600 to 2900 as well as on the short wave-length side of 2205 Å. Both band groups are characterized by the frequency difference 175 ± 5 cm.$^{-1}$. As and Sb show only a continuous absorption extending from the ultraviolet toward longer wave-lengths.

Spectral Classifications.—A 6-line multiple resulting from

* Communicated by the Director.

[1] Scientific Papers, No. 490. Price, ten cents.

the combination of 2 triplet p-terms was found among lines which are probably due to N^+. The spectra of As, Sb, and Bi contain doublet regularities. The valences of these elements are predominantly 3 and 5, and the valence one does not occur, suggesting that the arc spectra arise from transitions of one electron of a group of three which are more loosely bound than any others in the atom. In each element there is a group of low-lying energy levels which are separated from other levels by a gap of considerable magnitude. Classifications have also been obtained among the 14-volt lines of Bi. (Presumably lines of Bi^+.) To describe phenomena connected with the existence of very narrow doublet levels in Al^+ and Bi, as well as fine structures of spectral lines of Cu, Hg, and Tl, it is proposed to introduce a new quantum number, called the fine quantum number.

THEORY OF DETERMINATION OF ULTRA-RADIO FREQUENCIES BY STANDING WAVES ON WIRES.[2]

By August Hund.

[ABSTRACT.]

General Outline.—This paper furnishes the theoretical background for the method of frequency standardization employing short standing waves on parallel wires. The three essential differences between the parallel-wire systems employed by the Bureau of Standards for frequency standardization and the classical Lecher system are these: The waves produced are continuous instead of being damped, an electron-tube generating set being substituted for the spark-gap generating set; high-frequency voltages are impressed on the wires instead of being caused by discharge originating on the wires; a current-indicating instrument is used instead of a device for indicating voltage nodes.

The paper shows that the Bureau of Standards' method can be used for frequency standardization if the correction derived in the paper is employed in calculating the frequency.

The appendix of the paper gives the complete mathematical theory of standing waves on parallel wires with special reference to the system used at the Bureau of Standards. The main part of the paper gives the practical deductions that may be drawn from

[2] Scientific Papers, No. 491. Price, fifteen cents.

the mathematical theory, and also the method of calculating the correction to the frequency.

Essential Deductions from the Theory.—The basis of the frequency determination in the method under discussion is the direct measurement of the wave-lengths of very short waves on a pair of parallel wires. The frequency f is calculated from the formula

$$f = \frac{v_0}{2l}(1 - \Delta)$$

where $v_0 = 2.9982 \times 10^8$ per second is the velocity of light and l denotes the distance in metres between two consecutive maximum settings and the small quantity Δ is given in the paper in terms of the resistance and inductance of the wires at the frequency used. The corresponding wave-length in free space λ_0 in metres is $2l(1 + \Delta)$.

The waves used correspond to a frequency of 19,000 to 33,000 kilocycles per second. The measuring system consists of two parallel wires (0.145 cm. diameter, No. 15 A.W.G.) with a spacing of 4.2 cm. or some other suitable dimension. The ultra-radio frequency generating set is coupled to the closed end of the parallel wires. The distance l is measured by moving a shunted thermo-galvanometer, which is suspended between the two wires, along the wires until it shows a maximum indication of current. This galvanometer arrangement has a very low resistance. The point of maximum indication is marked on the wires as position *I–I* and the galvanometer moved still further along the wires until a second current maximum *II–II* is indicated. The distance *I–II* between these points of successive current maxima is equal to length l. If the parallel wires are sufficiently long a number of such points, such as *III–III*, *IV–IV*, etc., may be found. Measurements and theory show that the distance *II–III* is practically the same as the distance *I–II*. When many maximum conditions are used the settings farther out will not be as sharp, since the successive maxima decrease in the ratio 1 : 2 : 3 : 4 : 5, etc. The actual determinations are made with the positions *I–I* and *II–II* only since the distance l can be measured most accurately and the value obtained is reliable.

The discussion proves the following points:

(1) The parallel wire system can be used for primary fre-

quency standardization if a small correction is employed in calculating the frequency.

(2) The first two maximum settings are very sharp since they correspond to a condition of resonance and give a decided current maximum in each case.

(3) It is best to keep the parallel wires as short as possible and just long enough so that two maximum settings can be made. By connecting a small condenser across the input terminals, both maximum settings can be moved closer to the input end and without changing the distance *l* between them.

(4) The spacing between the wires and their size are accounted for in the correction term. Unless the spacing is chosen extremely small or extremely large, it has practically no effect on the distance between two consecutive maximum settings.

(5) A thermo-electric instrument which is shunted by a wire of low resistance does practically not affect the settings.

DEVELOPMENT OF A METHOD FOR MEASUREMENT OF INTERNAL STRESS IN BRASS TUBING.[2]

By Robert J. Anderson and Everett G. Fahlman.

[ABSTRACT.]

AN investigation recently completed by the Bureau of Mines deals with a new method for the quantitative estimation of longitudinal internal stress in tube shapes, *e.g.*, brass condenser or similar tubing. The various methods that have been applied for the quantitative determination of internal stress in wrought shapes of brass and other copper alloys were found not to be applicable to cold-drawn tubes since the stress in tubes is largely longitudinal. Circumferential stress may be present in tubes, depending upon the mode of manufacture, but longitudinal stress is invariably present. The presence of internal stress in brass tubes can, of course, be demonstrated qualitatively by treatment with an accelerating cracking agent, *e.g.*, a mercury-salt solution or ammonia, but this method is not sensitive to relatively low stresses.

The various methods suggested for stress detection in wrought shapes were applied to leaded brass tubes of the nominal composition 66.33 : 33.17 : 0.5 Cu-Zn-Pb, which had been reduced by cold work in the range 17 to 56 per cent. Stress could not be detected by accelerated cracking agents or by the usual cutting

[2] Technologic Papers, No. 257. Price, five cents.

methods, but it was known that stress was present because of warping which took place on maturing for long periods at the ordinary temperature. The experiments were carried out on tubes drawn with an internal mandrel.

In the tubes examined, it was found that the major stress is longitudinal, and that the stress in the outer portion of the tubing is a longitudinal tensile stress, while that in the inner part is a longitudinal compressive stress, the summation of the stresses being zero. Absence of circumferential stress in tubes is shown by the failure of diametrically cut rings to spring in or out on being slit in two.

The method described for measuring longitudinal internal stress in tubes is called the strip method, and is carried out by slitting a narrow strip longitudinally in a piece of tubing, *e.g.*, a strip 2.75 inches long and 0.10 inch wide in a 3.25-inch tube length, and then releasing one end of such a slit strip by cutting. Stress is indicated by the springing out of the freed end. The stress is calculated by a formula based on the modulus of elasticity of the material and the distance in movement of the freed end.

$$S = \frac{tEi}{l^2}$$

where S = internal stress, *i.e.*, the longitudinal stress,
t = thickness of the strip in inch,
E = modulus of elasticity of the material,
i = amount of springing out in inch, and
l = length of the cut strip.

The slit strip behaves like a beam loaded at one end, and the mathematical development of the formula required for calculating stress is given in the paper.

In the application of the method for determining the effect of low-temperature annealing (without appreciable softening) on stress release, in the case of a tube with longitudinal stress of about 12,000 lbs./in.^{2}, the stress was reduced about 10,000 pounds by heating for 2.5 hours at 325° C. with very small loss in hardness. It has often been thought that because cold-drawn brass tubes do not crack on application of an accelerating cracking agent that they are free from internal stress. The strip method is applicable for the quantitative estimation of stress inferior to those necessary to cause cracking under the application of mercurous nitrate. This method should be useful in control of manufacturing practice for tubes.

SATURATION RELATIONS IN MIXTURES OF SUCROSE, DEXTROSE, AND LEVULOSE.[4]

By Richard F. Jackson and Clara Gillis Silsbee.

[ABSTRACT.]

THE sugars, sucrose, dextrose, and levulose which constitute our adult sugar diet occur in commerce as solids, or sirups saturated, nearly saturated, or supersaturated. Sirups containing these sugars have been studied as phase rule systems. The solubility of sucrose is greatly diminished by the addition of invert sugar, but the total sugar content is greatly increased. Thus at 23.2° C., 100 g. of pure water dissolve 208.6 g. of sucrose, but 100 g. of water containing 151 g. of invert sugar dissolve only 158.2 g. of sucrose. At 30°, 100 g. water, 213.6 g. sucrose; while 100 g. water containing 160 g. invert sugar dissolve 168.4 g. sucrose. In these instances the total sugar dissolved by 100 g. of water is at 23.2° C., 309.2 g.; at 30°, 329.4 g. Dextrose and, by inference, levulose, exert almost exactly the same influence as invert sugar on the solubility of sucrose.

Similarly, dissolved sucrose diminishes the solubility of dextrose. A solution which at 30° C. contains 47.1 per cent. sucrose and 26.6 per cent. dextrose is saturated with respect to both sugars. In other words, it constitutes a quadruple point in this system at this temperature.

The presence of levulose diminishes but slightly the solubility of dextrose. With increased additions of levulose a solution is finally obtained which contains equal quantities of dextrose and levulose, such as the ordinary invert sugar solution. Such a solution is, however, saturated with respect to dextrose and its concentration with respect to invert sugar may for practical purposes be designated the "solubility of invert sugar." At 30° this sirup contains 69.7 per cent. of invert sugar as determined experimentally. From the solubility of dextrose it is possible to compute these "solubilities" at other temperatures; thus, 15°, 59.8 per cent.; 20°, 62.6 per cent.; 25°, 66.2 per cent.; 35°, 72.2 per cent.

Honey being mainly a solution of dextrose and levulose is directly comparable with this system. Assuming that honeys are stored at 20 to 25° C. the conclusion is reached that all are supersaturated with respect to dextrose. From the known solubilities

[4] Technologic Papers, No. 259. Price, ten cents.

the degree of supersaturation is shown to vary between 160 per cent. for the very fluid honeys to 290 per cent. for those in which the granulation has proceeded to complete solidification. From the statistical data a rough generalization is suggested which may make possible a prediction in regard to granulation if restricted to sirups of a similar degree of clarity.

A knowledge of the solubilities of sucrose in the presence of invert sugar and of invert sugar in the presence of sucrose makes possible a determination of the composition which is saturated with both. Such a sirup contains the maximum concentration which can be produced by the partial inversion of sucrose. Thus at 23.2° C. such a sirup should contain 36.3 per cent. sucrose, and 39.9 per cent. invert sugar; and at 30° C., 33.6 per cent. sucrose, and 45.4 per cent. invert sugar.

Methods of partial inversion of sucrose are reviewed. In tropical America the inversion is accomplished by addition of cane juice soured by acetic fermentation. The more scientific methods consist of enzymic inversion for cane juices and hydrochloric acid inversion for pure sugar free from any considerable inorganic impurities.

TESTS OF SOME GIRDER HOOKS.[8]

By Herbert L. Whittemore and Ambrose H. Stang.

[ABSTRACT.]

MILD-STEEL hooks having rectangular cross-sections are often used for lifting steel girders. Two hooks with their curved ends together are placed on a link carried by the crane hook.

Hooks of this kind are usually designed by combining the tensile and bending stresses. To determine the safety of hooks designed in this way, nine were tested, three each for the following loads: 5, 10 and 15 tons. The hooks were supplied by the mechanical engineering department of the American Bridge Company, Ambridge, Pennsylvania.

The hooks were loaded using several increments up to the proportional limit of the material, which was obtained from coupon specimens cut from each hook. The stresses on the inside and outside surfaces of the hooks were measured, experimentally,

[8] Technologic Papers, No. 260. Price, ten cents.

with strain gauges, having two-inch gauge lengths. Readings were taken along practically the entire length of each hook.

The stresses for the same gauge lines were also found, theoretically, by adding algebraically the stress due to the component of the load normal to a right section of the hook and the stress due to bending at that section. The bending stress was computed using the ordinary beam formula. The experimental and theoretical stresses were plotted for comparison in load-stress diagrams for each hook.

The maximum stresses in the hooks were also computed from the Winkler-Bach and the Andrews-Pearson formulas derived from theory of curved beams.

CONCLUSIONS.

(1) The stresses obtained from strain-gauge measurements on girder hooks of rectangular section agreed well with the stresses computed by the ordinary theory of combined tension and bending, except at the critical section.

(2) The experimental stresses at the critical section were higher than the values computed by the ordinary theory of combined tension and bending for all hooks except K-9. The results indicate that the Winkler-Bach and the Andrews-Pearson formulas, which take into account the curvature of the hook, give correct values for the stress.

(3) The stress computed by the Winkler-Bach and the Andrews-Pearson formulas was in no case more than 20 per cent. greater than the stress computed by the ordinary theory of combined tension and bending. If the factor of safety used in designing hooks of this kind is sufficiently large, it is believed that the use of the more exact formulas is not necessary.

(4) It is impossible to determine by visual inspection whether any part of the hook has been stressed beyond the proportional limit.

LOGGING AND SAWMILL CODE.[6]

[ABSTRACT.]

THIS code is one of a series of safety codes being prepared under the plan of procedure of the American Engineering Standards Committee. The Bureau of Standards accepted the sponsorship and the work has been carried on with the assistance of a representative sectional committee.

[6] Handbook No. 5. Price, sixty cents.

The code indicates methods of preventing accidents in the felling of trees and sawing into logs. The hazards of transportation of the log from the stump to the logging railroad or river are covered by a series of rules and recommendations.

Ground yarding, ground skidding, high-line skidding, use of log chutes, and snow and ice roading are among the methods of transportation covered.

Logging railroads are covered in considerable detail; specifications for weights of rail, spacing of ties, standard clearances, and guard-rail requirements are included. Standard hand, lantern, and flag signals and whistle code are also included as well as minimum requirements for steps and handholds on logging trucks.

River driving and rafting are included for use in the sections of the country where such work is still carried on.

As an appreciable percentage of logging accidents are due to the use or misuse of explosives, a few rules on the storage, transportation, and use of explosives are included. A group of rules on the transportation of inflammable liquids has been included because of the increasing use of internal-combustion engines for woods and mill operations.

The second part, which is devoted to sawmill operations, gives the requirements for mill layout, particularly as to machine arrangement and clearances, natural light and building exits.

The safety requirements for the unloading pond, and log conveyor are given in detail. These include requirements for pike pole handles, as statistics show that the breaking of pike poles has been responsible for a number of various serious accidents.

The guards to be installed about the head mill sawyer's stand and log carriage are enumerated, as are methods of guarding live rolls and their driving mechanisms.

Provisions for guarding edgers to protect operators against kickbacks are included. Guard barriers for trimmers and edgers are also required.

Special attention has been given to lath and shingle mills, which in the past have been responsible for many mutilated hands.

Transfer table, conveyors, and hog mills are also covered in some detail.

Part three deals with yard and kiln operations. A number of operating rules are included giving safe methods of handling lumber on piles.

Exit doors for kilns have been put in the requirements as a result of fatalities due to workmen being trapped in kilns inadvertently.

Other kiln rules deal with types of doors, ladders to roof, grade of tracks and protection of steam pipes in control pits.

Rules for the installation of lumber-handling machinery are included in this part.

Cross-reference is made to the Code for Safeguarding Power Transmission Apparatus for details of guards.

LARGE MOLLIER CHART FOR AMMONIA.[1]

[ABSTRACT.]

A LARGE size computing chart in foot-pound-Fahrenheit units has just been issued by the Bureau of Standards for the use of refrigerating engineers. This chart is reproduced full size from the drawing prepared for the reduced size chart already published as Miscellaneous Publication No. 52. It embodies the results of an extensive series of measurements of the thermodynamic properties of ammonia, which results have also been published in tabular form in Bureau of Standards Circular No. 142.

Numerous forms of such charts have been published for ammonia, steam, and other materials. The arrangement of the present chart is believed to possess certain advantages over previous forms. The coördinates are pressure (plotted to a logarithmic scale) as ordinates, and heat content as abscissa. The chart measures about 16 inches high by 40 inches wide, and can be read with greater accuracy and less eye-strain than the smaller size already published. Lines of constant entropy, volume, temperature, and quality are drawn on the chart. The chart is printed in black ink only. The arrangement is such that all lines are clearly distinguishable and can be readily recognized and followed, thus avoiding two-color printing and its attendant loss in accuracy.

Pressures and volumes can easily be read to an accuracy of 1 per cent., and heat content to within 0.5 B.t.u. By the use of the chart it is possible to analyze the processes occurring in a refrigerating cycle, and to determine, for example, the work of compression, the heat absorbed by the ammonia evaporated, the volume of the vapor at various stages of the cycle, etc. In all

[1] Miscellaneous Publication No. 57. Price, fifteen cents.

cases except where very accurate work is required, the chart is a complete substitute for tables of the properties of ammonia and results can be obtained from it with greater ease and speed than are possible with tables.

ELIMINATION OF WASTE—METAL LATH.[8]

[ABSTRACT.]

ELIMINATION of excess varieties of metal lath will undoubtedly prove of marked benefit to the manufacturers, distributors, and users of this commodity, and such is the general opinion of the representatives of the industry and allied interests who have formally accepted Simplified Practice Recommendation No. 3.

The proposals were originally set forth by the Associated Metal Lath Manufacturers at a general conference of the industry, convened at the Department of Commerce, under the auspices of the Division of Simplified Practice, on December 12, 1922. This recommendation, having sustained certain modifications to meet the complete approval of the industry, is now acceptable for publication in the department's " Elimination of Waste " series.

Prior to the simplification of varieties of metal lath, each manufacturer had issued his own individual specifications, and while the differences have not been radical, yet they have been enough to seriously confuse architects and builders. Not only has there existed a multiplicity of specifications, but the manufacturers were fabricating a multiplicity of varieties of metal lath. The specifications embodied in Simplified Practice Recommendation No. 3, and now acceptable to the trade, include nine different weights, thus fulfilling the modern industrial tendency to reduce the number of manufactured articles when no real service to the consumer is affected.

Simplified Practice Recommendation No. 3 effectively covers the following problems in construction work:

Attached ceilings, steel floor beams.
Attached ceilings under concrete (removable forms).
Attached to concrete ceilings (permanent forms).
Back-plastered metal lath stucco construction.
Beams and cornices.
Columns and pilasters.

[8] Simplified Practice Recommendation No. 3. Price, five cents.

Corner and jamb reinforcements in block partition construction.

Metal lath in steel joist construction.

Metal stud partitions, solid or hollow (fireproof buildings).

Overcoating stucco on metal lath.

Standing furring.

Stucco on metal lath over sheathing.

Suspended ceilings.

Wall furring.

Wood stud and joist construction.

The immediate net effect of this recommendation is a reduction from 125 varieties of metal lath to 24, corresponding to an 80.8 per cent. elimination. Furthermore, success in the effort of directing practice to a consolidation of certain weights, will raise the elimination percentage to 84.

FILES AND RASPS.*

[ABSTRACT.]

THE activities of the United States in meeting the many problems involved in its participation in the recent World War; the extent which it affected the material resources of the country; and the urgent necessity of the conservation of materials are some of the factors which prompted the immediate adoption of a program having as its primary object the elimination of useless varieties, sizes, and types of commodities.

Hardware and hand tools played a very important part in fabrication, and during August, 1918, the manufacturers of files and rasps were asked to confer with the conservation division of the War Industries Board with a view to reducing the excessive varieties then existing in the manufacture of these commodities. Data submitted by the manufacturers established the fact that files and rasps were being manufactured in 1351 varieties and that half the number would amply meet all requirements of the consuming trade. On August 1, 1918, as a conservation measure, a schedule of sizes and types was adopted by the manufacturers in coöperation with the War Industries Board which resulted in an elimination of 732 items and reduced their regular stock to 619 varieties. The success of this measure adopted and put into

* Simplified Practice Recommendation No. 6. Price, five cents.

effect during the war proved that many advantages were obtainable through reduction in varieties of products and the action of the manufacturers of files and rasps proved to be no exception.

During the week of September 11, 1922, a series of conferences was held at the Department of Commerce, under the auspices of the Division of Simplified Practice, with the manufacturers of hardware and hand tools with a view to simplification and elimination of waste. Files and rasps were considered at the preliminary conferences and those in attendance went on record favoring further reduction of varieties of these commodities. One of the outstanding results of this conference was the subsequent visit of a large manufacturer of files and rasps to the Department of Commerce to confer with the Secretary of Commerce and the Chief of the Division of Simplified Practice. This meeting evolved a definite program of simplification and formed the basis of a conference of all manufacturers interested, held in New York, N. Y., on February 1, 1923.

The conference on February 1, 1923, was attended by a group of the industry representing a large percentage of the production of files and rasps. The major question under discussion was the possibility of further reduction of varieties without detriment to the industry and the maintenance of a regular stock adequate to meet the demands of the consuming public. The deliberations of the conferees resulted in a unanimous recommendation to eliminate 165 additional items, said recommendation to be submitted to a general conference of representatives of manufacturers, distributors and users for consideration and acceptance.

On October 9, 1923, a report of the conference held in New York, N. Y., was submitted to the Division of Simplified Practice and as a result it was decided to call a general conference to consider the recommendations. The hardware convention scheduled for the week of October 15, 1923, at Atlantic City, afforded an excellent opportunity for this general conference and invitations were issued calling the meeting for October 17, 1923. The personnel listed on page 2 of this report supports the widespread interest in this constructive movement and is truly representative of manufacturers, distributors and consumers.

The recommendation, calling for an elimination of 165 odd sizes and types of files and rasps, was placed before the general conference and after discussion was unanimously adopted as a

standard of practice for the entire industry for a period of one year from the date of the final conference. A standing committee representing the three groups was also appointed to insure the adoption of the simplification embodied in the recommendation: To effect a greater degree of contact and coöperation between the Department of Commerce and the various manufacturers and organizations incident to the industry; and to consider periodic resurveys for constructive revision or substitutions.

Simplified Practice Recommendation No. 6 of the Department of Commerce contains the list of recognized types and sizes of files and rasps, together with the report leading up to this simplification.

NICKEL AND ITS ALLOYS.[10]

[ABSTRACT.]

THIS circular, which is a second and extensively revised edition of that first issued in 1921, is essentially a compilation of data obtained from many sources on the various properties and applications of nickel and its alloys and on the methods followed for their commercial production. Results obtained by different investigators on the properties of nickel and its alloys are presented in tabular and diagrammatic form.

Starting with a brief historical account of the development of the nickel industry following the discovery of this metal, the sources, metallurgy and refining of nickel and its production in various commercial forms and their uses and applications are discussed. The principal commercial application of nickel is in the manufacture of nickel steels, the consumption amounting to nearly three-quarters of the production. The larger part of the remainder is utilized in the manufacture of malleable nickel and of non-ferrous alloys, principally in combination with copper.

The chemical and physical properties of nickel are dealt with, together with a discussion of the relation of the physical properties to the composition and treatment of the material and also of the effect of the presence of certain impurities, such as carbon, manganese, sulphur, nickel oxide, and silicon, on the properties of nickel. The resistance to chemical corrosion of nickel has occasioned its wide use for chemical apparatus and equipment, and a growing adoption for cooking utensils. The tensile properties of

[10] Circular No. 100. Price, forty cents.

nickel at ordinary temperatures may range as follows: Tensile strength 50,000–110,000 lbs./in.^{2}, yield point 20,000–100,000 lbs./in.^{2}, the lower values being for the cast condition and the higher ones for the hard-rolled or drawn condition, while the elongation and reduction in area may be as low as 1 and 20 per cent., respectively, for the hard-rolled condition.

The technologic practices followed in the manufacture of nickel products, as casting, rolling, forging, annealing, welding and soldering, and electrodeposition are described.

The alloys of nickel and copper find wide commercial application, particularly Monel metal—an alloy containing about 67 per cent. nickel and 28 per cent. copper. The principal properties of Monel metal which render it of commercial value are resistance to corrosion and to erosion by water and steam and also to oxidation at higher temperatures up to about 800° C., strength and hardness, particularly at high temperatures, and the bright nickel finish which it takes and retains. Similar practices in manufacture hold, for the most part, in the case of Monel metal as for nickel. The physical properties of Monel metal are dealt with at length. The tensile strength of Monel metal at room temperatures may run from about 65,000 lbs./in.^{2} for the cast metal to 120,000 lbs./in.^{2} for the hard-rolled or drawn material; the rolled material shows at 500–600° C. about half this latter strength. Other copper-nickel alloys finding commercial use are cupronickel for bullet jackets, condenser tubes, etc., and nickel coinage for currency. The properties of "nickel silvers," which are copper-nickel alloys containing zinc and are used largely as substitutes for silver and as the base metal for plated silverware, are also discussed.

As already indicated, the alloys of nickel with iron, including nickel and nickel-chromium steels, constitute by far the most important commercial alloys containing nickel. Nickel and nickel-chromium steels are used mainly for structural purposes as bridges, automobiles, etc., and for guns, projectiles, and armor plate. The tensile properties of these steels are discussed in relation to the chemical composition and heat treatment received. Steels containing high percentages of nickel, 25 per cent. and higher, find use for gas-engine valves, boiler tubes, valve stems, electrical-resistance wire, and alloys of very low expansivity, such as invar and elinvar.

Nickel-chromium alloys find extensive use in the construction of electrical heating devices, rheostats or electrical resistances, and thermocouples. A table giving the chemical composition and properties of a large number of alloys containing nickel and used for electrical resistance is included. Nickel-chromium alloys in the form of castings and fabricated forms find much use for furnace muffles, carburizing and annealing boxes and tubes, and for other parts required to resist high temperatures.

Mention is made regarding the properties of many nickel alloys, including nickel-chromium, which show good acid-resisting qualities toward certain acids and solutions, depending on the nature of the alloy, and consequently find extensive application in the industries where exposure to chemicals and other corroding conditions is required.

Miscellaneous alloys containing nickel, including the light aluminum alloys, are briefly dealt with.

Some typical specifications for nickel alloys and an extensive bibliography are included.

UNITED STATES GOVERNMENT MASTER SPECIFICATION FOR FIRE-EXTINGUISHER LIQUID (CARBON TETRACHLORIDE BASE).[11]

[ABSTRACT.]

Federal Specifications Board Specification No. 36a.

THIS specification is a revision of Federal Specifications Board Standard Specification No. 36. It was prepared by a technical committee of the Federal Specifications Board. Before final approval the original specification was submitted to the Underwriters' Laboratories and to a large number of manufacturers of such products, whose suggestions were carefully considered. The original specification was promulgated as a government standard by the Federal Specifications Board on July 3, 1922. This revision was promulgated as a United States Government Master Specification by the Federal Specifications Board on June 1, 1924. It covers the grade of material, general requirements, detail requirements, methods of inspection and testing, and basis of purchase. The general requirements are: The liquid shall be capable of extinguishing fires caused by the burning of

[11] Circular No. 134 (2nd ed.). Price, five cents.

inflammable liquids and solids, shall be a non-conductor of electricity, and shall consist of carbon tetrachloride containing other suitable products necessary to produce a liquid conforming to the following requirements when tested according to the methods herein stated. The detail requirements are:

Appearance.—It shall be a clear, homogeneous, mobile liquid.

Specific Gravity.—The specific gravity at 15.5/15.5° C. shall be not less than 1.50.

Cold Test.—The liquid must have a cold test not higher than minus 45.5° C. (minus 50° F.).

Distillation.—Not over 2 per cent. shall distil below 60° C. At least 90 per cent. shall distil between 70° C. and 80° C. At least 99 per cent. shall distil below 100° C.

Impurities.—The liquid shall be free from nitrobenzene, water, acid, or alkali, and free halogens, and shall not contain more than 1.0 per cent. by weight of carbon disulphide. It shall not corrode brass, lead, or other material of equal corrosion-resisting properties.

Action of Dilute Alcohol on Human Subjects. W. R. Miles, Nutrition Laboratory, Carnegie Institution, Washington. (*Proc. National Academy of Sciences,* July, 1924.)—Doses of ethyl alcohol were given to five trained typists. The quantities taken varied from 21 to 42 grams per person and amounted to about .5 c.c. per kg. of body weight. The solutions employed contained the alcohol to the extent of from 14 to 22 per cent. Tests were continued for about four hours after ingestion, and showed an increase in typewriting errors of 39.3 per cent., a decrease in strokes per second of 2.6 per cent. and an increase in illegibility of 55 per cent., in comparison with previous performance.

From a group of nine men to whom 27.5 grams of alcohol were given in a 2.75 per cent. solution, it was found that the pulse-rate during rest was increased 8.8 per cent., that the temperature of the skin of face and hands rose respectively .2 and .7° C., that the amplitude of the patellar reflex was decreased 21 per cent., that the swaying of the body was increased 11 per cent. and that the coördination for pursuitimeter was less adequate by 14.3 per cent. "One entry (1 per cent. for electric threshold) represents an improvement over normal." From these and other experiments the conclusion is drawn. "For the pulse-rate during rest and during work, the metabolism and the skin temperature, the alcoholic effect is in the direction of increase as these factors are usually measured. Unless a specific dynamic action for alcohol be assumed, these changes, which definitely occur under the carefully controlled and routine con-

ditions of our experiments, apparently represent a decrease in organic efficiency due to the depressant action of ethyl alcohol, inasmuch as they are regularly associated with decreased reflex irritability, slower reaction, less keen, *i.e.*, higher sensory thresholds, slower muscular movements, less adequate and accurate muscular control, and less agile mental operations. The whole qualitative picture is one of decreased human efficiency as a quickly following result from the ingestion of this pharmacodynamic substance."

"Alcohol and Human Efficiency," Carnegie Institution, Publication No. 333, 1924, contains the full report on this subject.

G. F. S.

The Propagation of Explosive Waves. (*Comptes Rendus*, July 28, 1924.)—Last year the city of Lyons was laying down several kilometres of cast-iron pipe one metre in diameter. The author in 1890 had studied the propagation of sound waves and had reached the conclusion that very valuable information could be had from a study of the variations of air pressure at one point, produced as a wave ran along a pipe and back again after reflection. Interference fringes gave an inertia less registration of pressure changes. Two beams of light perpendicular to the axis were brought to interference on a registering cylinder. One of them travelled in a brass tube and was therefore not affected by pressure variations, while the other had its wave-length changed as the wave of sound caused the density of the air to change. Hence the fringes shifted as the wave passed and the cylinder preserved a record of the variation of pressure as a function of time. The observer had about 2 km. of pipe for his experiments. At least 19 passages of the same wave along the pipe were registered.

From the photographic records it is seen that the wave sent out by exploding fulminate of mercury raises the air pressure instantaneously to the maximum height. It is analogous to a water wave with a vertical front. The pressure then falls rapidly, after which there comes perhaps 30 small alternations of pressure that succeed one another at very brief intervals. They are probably due to air waves set up within the pipe by the walls shaken by the explosion. Even after several passages of the wave past the cylinder the sudden rise of pressure is maintained. Later it grows to be more gradual, as the wave is damped out.

The arrival of a wave set up by exploding gunpowder is indicated by a rather gradual rise of pressure succeeded by a fall at about the same rate, but after seven journeys past the recording point the front of the wave has become almost as steep as in the case of the fulminate. In the two explosions already considered, the end of the pipe was closed. When it was open, the record of a powder wave after reflection was the facsimile of what it was before reflection, except that condensations were converted into equal rarefactions.

G. F. S.

NOTES FROM THE RESEARCH LABORATORY EASTMAN KODAK COMPANY.*

AN INSTRUMENT FOR MEASURING THE SWELLING OF GELATIN ON RIGID SUPPORTS.[1]

By S. E. Sheppard and F. A. Elliott.

An instrument is described which measures the swelling of gelatin on rigid supports. It consists of a balance beam carried on the thrust block of a vertically mounted micrometer. One end of the balance beam has freely suspended from it a quartz-silica rod with a foot, the weight of the foot being compensated at the other end of the beam. The film, or plate strip, is held rigidly by clamps in a double-walled bath, through which water is circulated at constant temperature. The foot of the rod is adjusted to just rest in equilibrium on the surface of the gelatin layer. As swelling proceeds, the balance arm is tilted, the displacement is adjusted by the micrometer screw, and the difference in reading gives the swelling in millimetres. The probable error of single readings is about 0.01 per cent. A curve is shown which gives close agreement between the gravimetric determinations of swelling and those by thickness measurements.

NOTES ON THE PREPARATION OF STANDARD CELLULOSE.[2]

By A. B. Corey and H. Le B. Gray.

Several samples of cotton were purified according to the method proposed by the Cellulose Division of the American Chemical Society and compared with samples purified by modifying the original procedure. It was found that the method could be improved by omitting the bleaching process, with the result that a cotton could be obtained which contained as high as 99.8 per cent. α-cellulose. The method suggested by the writers consists of extracting the cotton with alcohol and ether, boiling for six

* Communicated by the Director.

[1] Communication No. 203 from the Research Laboratory of the Eastman Kodak Company and published in *J. Opt. Soc. Am.*, 9: 181, 1924.

[2] Communication No. 216 from the Research Laboratories of the Eastman Kodak Company and published in *Ind. Eng. Chem.*, 16: 853, 1924.

hours with a 1 per cent. solution of sodium hydroxide, and washing with distilled water. Cottons prepared in this way had a higher content of α-cellulose and lower cotton numbers than when bleaching solutions were used, showing that a bleaching operation is harmful in the preparation of a "standard" cellulose.

Reflection of Plane Polarized Light by Etched Metals. MISS OWEN JONES. (*Phil. Mag.*, July, 1924.)—Steels, brasses, aluminum-bronzes with copper-nickel, as well as pure metals—copper, bismuth, nickel and aluminum after having been polished and etched—were placed on the stage of a microscope. Plane polarized light from a nicol was sent down the tube of the instrument and was reflected normally from the specimen on the stage. The reflected light was received by a second nicol attached to the eyepiece. When the two nicols were parallel, rotation of the etched surface in its own plane through 360° caused each crystal to show two maxima and two minima of brightness. With the nicols crossed there are four maxima and four minima for each complete rotation. In some crystals manifesting this effect fine striations of the surface were visible under high magnification.

Suppose that the little furrows are of such shape that a plane cutting across them at right angles would display each to be a scalene right-angled triangle, with its hypothenuse on the main surface of the metal and with its right angle and the two sides meeting there located within that surface. Rays of light perpendicular to the surface, that is, to the hypothenuse, are reflected from the shorter side of the furrow to the longer side from which in turn they are reflected vertically upward. Vertical rays coming down upon the longer side are either thrown off to one side or are thrown upon the shorter side from which they are reflected vertically upward. The angle of 90° is assumed for the suppositious furrow because the light in the actual experiment is reflected normally by the etched surface. A mathematical examination of the polarization effects that should be found with such a series of parallel furrows as has been predicated shows that they would agree with the phenomena actually observed both with parallel and with crossed nicols. A massive model of the furrows was made by setting up pairs of blocks of various metals with 90° between the faces. These gave the same effects as crystals when they were treated in the same way.

With an alloy of Cu 94.8 per cent., Al 5 per cent. and P .2 per cent. an additional phenomenon was discovered. "As the stage was rotated under crossed nicols each crystal went through a definite colour series. The colours were much more marked if the analysing nicol was shifted slightly from its crossed position. The origin of the colours is not at present clear." G. F. S.

NOTES FROM THE U. S. BUREAU OF CHEMISTRY.*

THE ISOLATION AND PROPERTIES OF THE ALKALOIDS AND OIL OF LARKSPUR SEED (DELPHINIUM CONSOLIDA).[1]

By L. N. Markwood.

[ABSTRACT.]

THE pure oil of larkspur seed has been isolated and described. There have also been isolated two crystalline alkaloids, the compositions of which have been definitely established, and a third crystalline alkaloid, which has not yet been obtained in a pure state. Of the former two, delcosine ($C_{21}H_{33}NO_6$), melting point 198–199° C., is identical with a product previously obtained, while delsoline ($C_{25}H_{41}NO_8$), melting point 207–209° C., is an addition to the list of larkspur constituents.

THE OPTIMUM REACTION RANGES OF CROP PLANTS.[2]

By E. T. Wherry.

[ABSTRACT.]

STEPS are being taken to determine the optimum reaction ranges of important crop plants and methods of bringing the soil reaction of the land on which they are to be grown within this range. Previous experiments have yielded fictitious optimum reactions for individual plants, in that secondary physiological disturbances such as chlorosis have been caused by the methods used, but the effects of these disturbances have been concealed by the use of the pH method of stating reaction. The subject should be further studied by methods free from these objections.

A NEW MICROMELTING-POINT APPARATUS.[3]

By J. F. Clevenger.

[ABSTRACT.]

A NEW micromelting-point apparatus permits direct observation of individual crystals by the microscope while the melting point is being determined. Accurate melting temperatures up to 400° C. may be determined by the use of this apparatus.

* Communicated by the Chief of the Bureau.

[1] Published in *J. Am. Pharm. Asso.*, **13** (Aug., 1924) : 696.

[2] Published in *Ind. Eng. Chem.*, **16** (Aug., 1924) : 826.

[3] Published in *Ind. Eng. Chem.*, **16** (Aug., 1924) : 854.

THE DETERIORATION OF SOAP-NICOTINE PREPARATIONS.[4]

By C. C. McDonnell and E. J. Nealon.

[ABSTRACT.]

SHORTAGE of nicotine in soap-nicotine preparations as ordinarily found on the market led to an investigation of the ingredients, preparation, and methods of packing this product, which is used as an insecticide.

The nicotine content of hard soda soaps decreases very rapidly, but little or no change takes place in the nicotine content of soft soda or potassium soaps.

Retention of nicotine apparently depends on the physical condition of the soap; its decrease is attributed to chemical changes, probably also involving the fatty acids of the soap, and not to loss by volatilization.

Lightning Rods on Farms. (U. S. Department of Agriculture, Clip Sheet No. 326.)—For more than thirty years the Weather Bureau has been an earnest advocate of the protection of buildings and other property against lightning by suitable rodding. The bureau is frequently called upon to advise inquirers concerning the proper methods and materials to be employed. Occasionally plans are drawn up in detail for the protection of government structures. In 1910 the White House was rodded after plans and specifications prepared by Professor Marvin.

To determine the relative liability of farm buildings to fire damage by lightning, a study of lightning fire losses was made recently by the Weather Bureau of the United States Department of Agriculture. The average annual loss for the whole United States is a little over $12,000,000 which is probably a conservative figure. Illinois has the unenviable first place, with an average annual loss of over a million dollars, part of which may be attributed to industrial sections. Texas is next in order because of its large area and the presence of highly inflammable oil-storage tanks. New York is third, for reasons similar to those affecting Illinois. In the highly developed agricultural states of the North heavy losses are suffered, especially through destructive cyclonic thunder-storms. If the index number showing relative liability of farm buildings to damage is small in one state when compared with another having equally destructive and frequent thunder-storms, it is quite probable that protection against lightning is more general in the former state. Michigan, Wisconsin, Minnesota, and Iowa are states where it is estimated that somewhat more than half of the farm buildings are protected by rodding. R.

[4] Published in *Ind. Eng. Chem.*, 16 (Aug., 1924): 819.

NOTES FROM THE U. S. BUREAU OF MINES.*

SPONTANEOUS COMBUSTION OF COAL.

By J. D. Davis.

EXPERIMENTS in the spontaneous heating of coal in presence of an excess of oxygen were conducted under such conditions that all of the heat generated by oxidation of the coal was employed in raising its temperature. This was done in order that the rates of heating would be a measure of the tendency for spontaneous heating of the coal. All the coals treated were ground to 100 mesh. It was found that (1) the tendency to heat was greater for coals high in oxygen than for coals low in oxygen, although not directly proportional to the oxygen content; (2) the heating tendency of coals of similar rank was approximately the same; (3) the rate of generating heat in spontaneous combustion is directly proportional to the amount of oxygen used.

Further details are given in a paper presented before the meeting of the American Chemical Society at Ithaca, New York, September 8, 1924.

FILTER SAND FOR MUNICIPAL WATER SUPPLY.

By M. W. Weigel.

THE use of sand for the filtration of municipal water supplies is of comparatively recent use in this country, although at the present time, most cities of any size that draw their water supply from surface sources use sand filters in their purification system. Not only are sand filters employed to remove sediment and suspended matter, but they also take out most of the bacteria in the water.

The writer recently completed a study of filter sand, its requirements, specifications and methods of mining and preparation.

The general requirements for filter sand are more exacting than for any of the different kinds of sands, except the chemical specifications for glass sand. Filter sand must be uniform in size and within certain limiting sizes. In addition, it must be

* Communicated by the Director.

clean and free from clay and organic matter and of fairly high purity. There is no requirement as to grain shapes, except that they be not flat or elongated, since, so far as known, either rounded or angular grains are equally efficient. A fuller description of the results of this study is given in Serial 2622.

THE UTILIZATION OF DOLOMITE FOR REFRACTORIES.

By G. A. Bole.

THE dolomite refractories investigation of the bureau includes a study of the many fluxes which could be used to aid in the dead-burning of dolomite and also a complete survey of the iron oxide-alumina-silica field as fluxes. The temperature of calcination and the resulting properties have been carefully investigated, and the most desirable calcines chosen for further investigation in the making of dolomite bricks. Many binders and the several methods in common use of fabricating bricks commercially were tried, and a thorough study was made of the properties of the most successful ware. A review of the work done by the bureau's investigators is presented in Serial 2627, recently issued.

DETERMINATION OF GAS DISTRIBUTION IN INTERNAL-COMBUSTION ENGINES BY GAS ANALYSIS.

By G. W. Jones, W. P. Yant, and L. N. Berger.

GAS analysis is of great practical value to the combustion engineer as a guide in the proper design and operation of power and heating plants. The automotive industry, however, has made little use of gas analysis in the design and construction of engines. Tests made by the Bureau of Mines have shown that for the average motor vehicle approximately 30 per cent. of the heat value of the gasoline passes out in the exhaust as incomplete-combustion products. Gas analysis enables the engineer to determine the quality of the mixture fed to the different cylinders with a high degree of precision. Briefly, the method consists in making an analysis of the exhaust gas from each cylinder while the engine is in operation.

Automobile exhaust gas is a complex mixture of gases consisting mainly of carbon dioxide (CO_2), carbon monoxide (CO), oxygen (O_2), methane (CH_4), hydrogen (H_2), and nitrogen

(N_2), and at times gasoline vapor and traces of unsaturated hydrocarbons. A complete analysis of the gas requires the services of an experienced gas chemist and a rather complicated apparatus.[1] However, for the determination of distribution, a complete analysis of the exhaust gas is not necessary. All that is required is the percentage of carbon dioxide in the exhaust and the total carbon dioxide in the gas after the sample is burned in a slow-combustion pipette. The authors have developed a simple portable apparatus for making this determination. The apparatus for making this determination consists of a 100-c.c. measuring burette, a caustic pipette, and a slow-combustion pipette. It is easy to manipulate, and dependable results may be obtained by an unskilled technician.

To determine the total carbon-containing gases in the exhaust from each cylinder, a measured volume of the exhaust gas is passed into the slow-combustion pipette containing an excess of air, and the combustibles are burned to carbon dioxide. The total percentage of carbon dioxide in the sample after this combustion gives the relative amount of fuel introduced. From the percentages thus found in the exhaust from the different cylinders the relative distribution can be obtained directly.

Tests were conducted and charts prepared which show how the relative distribution of fuel to the different cylinders of an internal-combustion engine can be determined by gas analysis. Also, tests were made showing results obtained from an engine having good distribution, and tests made under road conditions on an engine giving poor distribution. For a more complete discussion the reader is referred to Serial 2631, recently published by the bureau.

Industrial Accidents to Working Minors.—Seven thousand four hundred and seventy-eight industrial accidents to young workers under twenty-one years of age occurred in one year in three states, according to a study just completed by the Children's Bureau of the U. S. Department of Labor.

Thirty-eight of these accidents resulted in death and 920 in partial disablement for life.

Wisconsin, Massachusetts and New Jersey were the states

[1] This has been described in a previous article on "Sampling and Analysis of Automobile Exhaust Gases," by A. C. Fieldner and G. W. Jones, published in the Jour. Frank. Inst., vol. 194, 1922, p. 613.

included in the study. The cases of industrial accidents to minors were secured from the files of State Industrial Commissions and Accident Boards and were only those in which compensation had been paid; that is, in Wisconsin, accidents causing disability of more than seven days' duration; in Massachusetts and New Jersey, accidents causing disability of more than ten days' duration.

The smallest number of accidents and the lowest accident rate occurred in the case of children under sixteen. Each of the states studied had attempted to protect children under this age by prohibiting them from employment in certain occupations, chiefly in the operation of the more dangerous machinery, which is the source of greatest accident hazard to the young worker.

Children of sixteen and seventeen were prohibited from some employments in Massachusetts and Wisconsin but in all three states were permitted to operate many of the dangerous machines.

Accident figures reflected this difference in legal protection. Power-working machinery caused a larger percentage of the accidents to the 16- and 17-year-old group than to children under sixteen—protected by law—or to young workers between eighteen and twenty-one—better able to protect themselves.

Accidents were also more serious to the 16- and 17-year group than to either the younger or older workers. Of the injuries to workers under sixteen, 10.7 per cent. resulted in death or partial disablement for life. For those sixteen and seventeen years old who were injured, the rate was 13.4 per cent. killed or permanently disabled; for the group 18-21 years the rate was 12.7 per cent. R.

Electroplating.—According to data collected by the Department of Commerce at the biennial census of manufactures, 1923, the establishments engaged primarily in electroplating reported products valued at $12,243,133, an increase of 52.3 per cent. as compared with 1921, the last preceding census year. The establishments classified in this industry to some extent do work on material furnished by others, and the value of products in such cases is the amount they received for work performed.

In addition to the products reported in the classified industry many establishments making jewelry, plated ware, and other articles electroplate their own wares, but the cost of such work is not reported separately.

Of the 440 establishments reporting for 1923, 101 were located in New York, fifty-three in Illinois, thirty-seven each in Massachusetts and Ohio, thirty-five in Pennsylvania, thirty-three in California, twenty-three in New Jersey, fourteen in Missouri, thirteen each in Indiana, Michigan and Rhode Island, twelve in Wisconsin, eleven in Connecticut, eight in Maryland, seven in Minnesota, six in Texas, and the remaining twenty-four in Alabama, Colorado, Delaware, District of Columbia, Georgia, Iowa, Kentucky, Montana, Nebraska, Oregon, Tennessee, and Washington. R.

THE FRANKLIN INSTITUTE.

MEMBERSHIP NOTES.

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(Stated Meeting, Board of Managers, September 11, 1924.)

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DR. ANCEL ST. JOHN, Consulting Physicist, 17 Hix Avenue, Rye, New York.

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MR. H. H. VAUGHAN, 285 Beaver Hall Hill, Montreal, P. Q., Canada.

NECROLOGY.

Mr. Charles Wm. Masland, 3240 Amber Street, Philadelphia, Pennsylvania.

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BOOK REVIEWS.

COAL CARBONIZATION. By Horace C. Porter, M.S., Ph.D. 442 pages, 175 illustrations, charts, 8vo. New York, The Chemical Catalog Company, 1924. Price, $6.

This is a monograph of the American Chemical Society's series uniform with those previously issued. The author is a chemical engineer. The subject is one of comparatively long development, as compared with many other departments of chemical engineering. Professor Parr, of the University of Illinois, observes in the preface that the centennials of Murdoch's and Lebon's establishment of the gas industry in England and France, respectively, have just been celebrated. In the United States, the introduction of gas dates from only a little more than a century ago, and for three-quarters of that period little improvement was made in the procedures. This lack of development may have been largely due to the comparative simplicity of the operations. If we look closely at the history of gas manufacture, we will, however, find some marked advances in what may be termed side issues, yet affecting the basic industry. The utilization of the tar and wash liquors not only added to the economies of operation but ameliorated very much the offensive character of the procedures. The substitution of iron oxide for lime in desulphurizing was also a step of importance. The initial use of gas was as an illuminant. Its application for heating especially in cooking and its use in the internal combustion engine have been much later developments, and they have saved the gas industry as a going concern, for there is little doubt that its use as an illuminant is rapidly declining. The electric lamp has taken its place.

A very decided modification of the illuminating gas industry occurred when water-gas was introduced. This, depending on entirely different principles than the standard gas production, caused changes not only in gas engineering, but in matters of public hygiene. The old-fashioned "coal-gas" was but mildly toxic. Persons breathing it for some time would, of course, be asphyxiated, but rarely fatally. Simple and well-known restorative methods would bring back consciousness. It is a familiar melodramatic story that, when the introduction of gas was originally proposed in Philadelphia, a committee of prominent citizens protested strongly against it, alleging, among other things, that if the gas works should take fire the whole city would be blown up! It was the irony of fate that one of the signers of this protest was afterwards chief engineer of the works. When it was proposed to introduce water-gas into the city supply a protest of physicians was made, and the newspapers, of course, made merry over the matter, reprinting the old protest. The later protest, however, was based on the danger from the poisonous character of carbon monoxide, which is a prominent ingredient of water-gas, and the records of mortality in cities in which such gas is used served amply to justify the warnings that the Philadelphia physicians gave.

It is gratifying to see a book of this character, for it gives hope that more extensive coal-carbonization industries will be established. Much advantage results to the community at large by the substitution of coal carbonization for the water-gas process. The treatment of coal gives as by-products,

coke—an excellent fuel, a valuable tar, ammonia and an illuminant low in carbon monoxide.

The book gives a comprehensive account of the present state of the industry, both in the form in which the volatile products are utilized and those in which the coke is the object sought. Perhaps the most interesting part is that which deals with the problem of house heating by gas. The 1923 Committee of the American Gas Association on "Rate Structure," referred to house heating as one of the big opportunities for gas works. One practical difficulty is the great increase of load that would result in the cold season. In our northern cities, the demand except for cooking, is very low through about five months, but would become enormous during the other parts of the year. The present distribution installations in our cities could not meet this demand. Yet it is to be devoutly hoped that engineering talent will be brought to bear on this problem, and the housekeeper relieved from coal-bin and ash-can woes. Oil, of course, looms up in this relation, but the installations are more complicated than gas heating might be, and the supplies of oil are not as abundant as those of good gas coal.

Doctor Porter's book will be of great value to the engineers connected with all departments of fuel industries. HENRY LEFFMANN.

THE PLANT ALKALOIDS. By Thomas Anderson Henry, D.Sc., Director, Wellcome Chemical Research Laboratories. Second edition, viii–456 pages, 8 plates, 8vo. Philadelphia, P. Blakiston's Son and Company, 1924. Price, $8.50.

The term "alkaloid" is given in a quotation in the New English Dictionary (Murray) as originating in Germany. Its etymology is obvious. Sertürner of Paderborn was the first to extract from a crude drug, a concentration that contained the main active principle. He worked with opium. His earliest efforts were in the first decade of the nineteenth century, but it was some time before he had definitely established the nature of the substance, which he named "morphin." Some claims have been made for a French investigator, "Citizen" Derosne, who, however, does not seem to have a claim over Sertürner. The publication of the latter's work aroused general interest, other crude, potent drugs were examined, and a considerable number of substances similar in composition to morphin and having the marked basic power were discovered. For two decades or so, all substances of this type were obtained from plants, existing ready formed in some of the tissues thereof. In 1834, Runge obtained quinolin from coal-tar, and in 1846, Anderson obtained pyridin from Dippel's animal oil. Speculation as to the structure of the alkaloids has not led to definite results. Containing nitrogen, they were naturally regarded as related to ammonia. In 1848, Wurtz discovered the compound ammonias, but comparison of these with most of the alkaloids was unsatisfactory, as the latter contain notable amounts of oxygen.

Research slowly elucidated the problems and it has been found that several classes of alkaloidal structure exist and that the closed chain structure is frequent.

The present work gives a comprehensive account of all important alkaloids of natural origin, explaining the structure of each, as far as known, and

detailing properties and tests. Much of the work has been rewritten as much new matter had accumulated since the first issue. Methods of determination of alkaloids have been somewhat abbreviated, as the author believes that this part of the field is well covered by existing analytic manuals. Some specific attention has been given to the determination of the relation of chemical structure to physiologic action, but Doctor Henry expresses the correct view that while many observations have been made on the subject in connection with the alkaloids, no general conclusions can yet be drawn.

In the field of analysis, a great deal of experimenting has been done with a view to employing the refractive-index method to the detection of the crystallized alkaloids and their salts, but serious difficulties of manipulation have so far interfered with progress. This phase is, of course, entirely outside the scope of the book. The book is a valuable addition to the literature of a subject of great interest and importance in both theoretical and practical relations.

HENRY LEFFMANN.

ALLEN'S COMMERCIAL ORGANIC ANALYSIS. Volume II. Fifth Edition, revised and in part rewritten. Edited by Samuel S. Sadtler, B.S., and Elbert C. Lathrop, A.B., Ph.D., and C. Ainsworth Mitchell, M.A., F.I.C., assisted by collaborators. ix–807 pages, 8vo, illustrated. Philadelphia, P. Blakiston's Son and Company. Price, $7.50.

It is now nearly fifty years ago that the first edition of this work appeared and offered to practising analysts a most welcome aid. Up to that time little information on many points in the development of industrial organic chemistry was available to English-speaking chemists. The book as it came from Mr. Allen's hands represented not only an extensive experience in his own laboratory, but a comprehensive and careful search in the literature. The work took at once front rank among manuals of analysis, has maintained that position without interruption to the present time, and may be expected to continue its fame for many years. The author has long since passed away, but his "wonted fires" still illuminate the later editions. The development of industrial organic chemistry has been such as to render the two volumes of the first edition far insufficient for the materials, and the work grows steadily in volume, until it assumes the appearance of an encyclopædia.

This volume in hand covers the fats, fixed oils and waxes and is an exhaustive treatise on these topics. The selection of specialists from both England and America gives a broader tone to the book and makes it serviceable in a wider field. There is a tendency in modern works on industrial analysis to enter rather largely into the technology. Some such treatment is needed, for the nature of adulterants of products will depend a great deal on the manner in which they are made, but the two fields are essentially distinct, and editors should not allow a notable admixture. In the present work the essential purpose of the book—analytical—is well maintained.

This being a fifth edition, it is unnecessary to speak at great length of its merits. "Allen" is so well known, and the editors and collaborators of the present volume are so fully recognized as capable of the tasks assigned to them, that little is required except to note the publication. In Editor Mitchell's account of the Reichert-Meissl method, the long and elaborate description of

the procedure is given, and it is stated that the glycerol-soda method (which is much simpler and equally trustworthy for practical purposes) is "the official German method." As a matter of fact, it is now an official method in the United States, and also in France and Italy. This fact should not have been overlooked by the American editors, but the omission is of no great importance, since every American chemist, who is at all familiar with the volatile acid determination as a datum in fat analysis, knows the process and has used it.

Chemists are much pleased to greet the second volume of the new edition and hope to see the complete revision make rapid progress.

HENRY LEFFMANN.

NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS. Report No. 187, Flame Speed and Spark Intensity, by D. W. Randolph and F. S. Silsbee. 14 pages, illustrations, quarto. Washington, Government Printing Office, 1924.

This report describes a series of experiments performed at the Bureau of Standards under the auspices of the Committee. These experiments were undertaken to determine whether or not the electrical characteristics of the igniting spark have any effect on the rapidity of flame spread in the explosive gas mixtures which it ignites. The results show very clearly that no such effect exists. The flame velocity in carbon-monoxide-oxygen, acetylene-oxygen, and gasoline-air mixtures was found to be unaffected by changes in spark intensity from sparks which were barely able to ignite the mixture up to intense condenser discharge sparks having fifty times this energy.

Report No. 189, Relation of Fuel-Air Ratio to Engine Performance, by Stanwood W. Sparrow. 16 pages, illustrations, quarto. Washington, Government Printing Office, 1924.

The purpose of this investigation was to ascertain from engine tests the answers to the following questions:

(1) What gasoline-air ratio gives maximum power?

(2) Is the value of this ratio appreciably affected by such changes in air-pressure or temperature as are encountered in flight?

(3) What percentage of its maximum power does an engine develop when supplied with a mixture giving minimum specific fuel consumption?

This report was prepared for publication by the Committee and the tests upon which it is based were made at the Bureau of Standards between October, 1919, and May, 1923. From these it is concluded that: (1) With gasoline as a fuel, maximum power is obtained with fuel-air mixtures of from 0.07 to 0.08 pound of fuel per pound of air; (2) maximum power is obtained with approximately the same ratio over the range of air-pressures and temperatures encountered in flight; (3) nearly minimum specific fuel consumption is secured by decreasing the fuel content of the charge until the power is 95 per cent. of its maximum value.

Presumably this information is of most direct value to the carburetor engineer. A carburetor should supply the engine with a suitable mixture. This report discusses what mixtures have been found suitable for various engines. It also furnishes the engine designer with a basis for estimating how much greater piston displacement an engine operating with a maximum economy mixture should have than one operating with a maximum power mixture in order that both may be capable of the same power development.

Report No. 192, Charts for Graphical Estimation of Airplane Performance, by Walter S. Diehl. 12 pages, illustrations, quarto. Washington, Government Printing Office, 1924.

This report, which was prepared at the request of the Committee, contains a series of charts which were developed in the Bureau of Aeronautics of the Navy Department in order to simplify the estimation of airplane performance. Charts are given for estimating propeller diameter and efficiency, maximum speed, initial rate of climb, absolute ceiling, service ceiling, climb in ten minutes, time to climb to any altitude, maximum speed at any altitude, and endurance. A majority of these charts are based on the equations given in N.A.C.A. Technical Report No. 173. Plots of pressure and density against altitude in standard air are also given for convenience. It must, of course, be understood that the charts giving propeller diameter, maximum speed, initial rate of climb, absolute ceiling, and speeds at altitudes are approximations subject to considerable error under certain conditions. These particular charts should not be used as a substitute for detailed calculations when accuracy is required, as, for example, in military or naval proposals.

PUBLICATIONS RECEIVED.

Coal Carbonization. By Horace C. Porter. 442 pages, illustrations, 8vo. American Chemical Society Monograph Series. New York, The Chemical Catalog Company, Incorporated, 1924. Price, $6.

Allen's Commercial Organic Analysis. Fifth Edition, Volume II. 807 pages, 8vo. Philadelphia, P. Blakiston's Son and Company, 1924. Price, $7.50.

The Plant Alkaloids. By Thomas Anderson Henry. Second Edition. 456 pages, illustrations, plates, 8vo. Philadelphia, P. Blakiston's Son and Company, 1924.

Il Gruppo Società Adriatica di Elettricità ed il Progresso dell' Industria Elettrica nella Regione Veneto-Adriatica Durante l'Ultimo Decennio. Società Adriatica di Elettricità, Venezia. 88 pages, illustrations, folio. Venice, Society, 1924.

U. S. Department of Commerce. Elimination of Waste: Simplified Practice: Bed Blankets, Cotton, Wool, and Cotton and Wool Mixed. 7 pages, 8vo. Washington, Government Printing Office, 1924.

U. S. Bureau of Standards. Scientific Papers, No. 491, Theory of Determination of Ultra-radio Frequencies by Standing Waves on Wires, by August Hund. 54 pages, figures, quarto. Technologic Papers, No. 259, Saturation Relations in Mixtures of Sucrose, Dextrose, and Levulose, by Richard F. Jackson and Clara Gillis Silsbee. 28 pages, figures, quarto. Washington, Government Printing Office, 1924.

U. S. National Advisory Committee for Aeronautics. Technical Notes, No. 199, Micarta Propellers II—Method of Construction, by F. W. Caldwell and N. S. Clay. 8 pages, photographs, figures, quarto. No. 200, Micarta Propellers III—General Description of the Design, by F. W. Caldwell and N. S. Clay. 10 pages, photographs, figures, quarto. No. 201, Micarta Propellers IV—Technical Methods of Design, by F. W. Caldwell and N. S. Clay. 8 pages, figures, quarto. Washington, Committee, 1924.

CURRENT TOPICS.

Forest Fires in Outdoor Laboratory. (U. S. Department of Agriculture, Press Service, September 11, 1924.)—Study of the foes of the forest is fully as important as the study of its reproduction, growth and management, in the view of the United States Forest Service. One great enemy of the timber grower in every thickly wooded section of the country is fire, and, therefore, in its great outdoor laboratories in nearly every important forest region in the United States, the Forest Service studies the action of fire as carefully as questions of soil, moisture, or forest planting.

"To all those in the South who live in our woodlands and cut-over lands," states Director R. D. Forbes, of the Southern Forest Experiment Station, "the damage caused by fires is apparent enough. Not only do they see large standing trees destroyed, as the result of repeated injury from fire through a number of years, but they note as well that timber growth is stunted and that, worst of all, the young seedlings that should begin to form the new generation of the forest are completely wiped out. Unfortunately, however, people in the city and in agricultural districts where fires are infrequent in such woodlands as still exist do not realize as keenly as the people of the piney woods what damage is caused by fires. They do not understand why we keep warning people of the necessity for protecting the forest areas of the South from all fires.

"In order to convince all the people of the importance of fire protection we must have a fairly exact measure of fire damage, which can be expressed definitely in cords of wood or thousands of board feet."

Here the laboratory work comes in, we are told. The Forest Experiment Station proceeds to stage its own forest fires. By laying off small areas of growing timber of various ages and burning proportions of them deliberately at different seasons of the year, at the same time leaving similar areas in the "rough" for comparison, the foresters can keep a yearly record of the damage that fires do to all sorts of timberland. But a forest laboratory needs time as well as space in more liberal portions than the indoor laboratory. These studies, now being made in stands of all four of the important pines of the South, will take a number of years to complete, Director Forbes announces. While some information of real value has already been obtained, it will be probably another decade before anything like final results can be promised. R.

Iron and Steel Doors and Shutters.—Establishments engaged primarily in the manufacture of iron and steel doors and shutters in 1923 reported such products valued at $14,077,428, together with

other classes of products valued at $1,289,683, making a total of $15,367,111. The rate of increase in the total value of products as compared with 1921, the last preceding census year, was 23.3 per cent.

In addition, doors and shutters were manufactured to some extent as secondary products by establishments engaged primarily in other industries. The value of these products thus made outside the industry proper in 1921 was $386,457, an amount equal to 3 per cent. of the total value of products reported for the industry proper. The corresponding value for 1923 has not yet been ascertained but will be shown in the final reports of the present census.

Of the thirty-seven establishments reporting for 1923, twenty-two were located in New York, four in Illinois, and the remaining eleven in California, Indiana, Minnesota, Missouri, New Jersey, Ohio, and Tennessee. In 1921 the industry was represented by forty-five establishments, the decrease to thirty-seven in 1923 being the net result of the omission of ten establishments which were included in 1921 and the inclusion of two new establishments. Of the ten establishments omitted, four had gone out of business before the beginning of 1923, one was idle throughout the year, four had been engaged primarily in the manufacture of doors and shutters in 1921 but reported other commodities as their principal products in 1923 and were therefore classified in the appropriate industries, and one reported products valued at less than $5000 in 1923. These data are announced by the Department of Commerce in connection with the biennial census of 1923. R.

Cash Registers and Calculating Machines.—The establishments engaged primarily in the manufacture of cash registers and calculating machines reported products valued at $95,105,570, an increase of 77.3 per cent. as compared with 1921, the last preceding census year. The classification covers adding machines, cash registers, calculating, and computing machines, and automatic ticket selling devices. These data have been collected by the Department of Commerce for the biennial census, 1923.

Of the thirty-seven establishments reporting in 1923, seven were located in Michigan, six each in Illinois, New York, and Ohio, and the remaining twelve in California, Connecticut, Iowa, Massachusetts, Missouri, New Jersey, Pennsylvania, Rhode Island, and Wisconsin. In 1921 the industry was represented by forty-nine establishments, the decrease to thirty-seven in 1923 being the net result of the omission of seventeen establishments which had been included for 1921 and the inclusion of five which had not been classified in this industry for 1921. Of the seventeen establishments omitted, seven had gone out of business prior to the beginning of 1923, two were idle during the entire year, six had been engaged primarily in the manufacture of cash registers and calculating machines in 1921 but reported other commodities—paper goods; clocks and clock move-

ments; carriages, wagons, sleigh and sled materials; and foundry and machine shop products—as their principal products for 1923 and were therefore classified in the appropriate industries, and two reported products valued at less than $5000 in 1923. (No data are tabulated at the biennial censuses for establishments with products under $5000 in value.) Of the five establishments not previously classified in this industry, four were new to the census and one had been engaged primarily in the manufacture of other commodities such as foundry and machine shop products in 1921. R.

Aircraft.—The data collected at the biennial census of manufactures, 1923, by the Department of Commerce, indicate that the establishments engaged primarily in the manufacture of aircraft produced 505 airplanes valued at $6,166,218 and 82 seaplanes and flying boats valued at $1,570,851, together with other products to the value of $5,208,194, making a total of $12,945,263. The rate of increase in this total as compared with 1921, the last preceding census year, was 94.9 per cent.

In addition, airplanes, seaplanes, and parts were made to some extent by establishments engaged primarily in other industries. The value of such planes and parts thus produced outside the industry proper in 1921 was $777,843, an amount equal to 11.7 per cent. of the total value of products reported for the aircraft industry. The corresponding value for 1923 has not yet been ascertained, but will be shown in the final reports of the present census.

Of the thirty-three establishments reporting for 1923, twelve were located in New York, four each in California and Ohio, three in Illinois, and the remaining ten in Connecticut, Maryland, Michigan, Nebraska, New Jersey, Pennsylvania, Rhode Island, Washington, and Wisconsin. R.

Aluminum Manufactures.—The Department of Commerce announces that, according to data collected at the biennial census of manufactures, 1923, the establishments engaged primarily in the manufacture of aluminum castings, bars, plates, sheets, ware, etc., reported products valued at $106,930,367, an increase of 133.4 per cent. as compared with 1921, the last preceding census year.

Of the 119 establishments reporting for 1923, twenty-seven were located in Ohio, fourteen in Wisconsin, twelve in Michigan, eleven in New York, nine in Illinois, seven in New Jersey, six each in Indiana, Massachusetts, and Pennsylvania, five in California, and the remaining sixteen in Colorado, Connecticut, Iowa, Minnesota, Missouri, Nebraska, Rhode Island, Tennessee, and Washington. R.

PRESS OF
J. B. LIPPINCOTT COMPANY
PHILADELPHIA